SOIL AND GROUNDWATER REMEDIATION GUIDELINES FOR METHANOL

December 2010

Government of Alberta

ISBN No. 978-0-7785-9009-5 (Printed Edition)
ISBN No. 978-0-7785-9010-1 (On-line Edition)
Web Site: http://environment.gov.ab.ca/info/

Soil and Groundwater Remediation Guidelines for Methanol
December 2010

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1. INTRODUCTION

Methanol is an industrial chemical with a wide range of uses as a chemical feedstock, solvent and fuel. It is also used in the upstream oil and gas industry for hydrate inhibition in natural gas production and transport, removal of acid gasses, as a dehydration agent, in the recovery of heavy hydrocarbons, and in the pressure testing of pipelines and pressure vessels in cold temperatures. Any of these uses may result in the release of methanol into the environment. Common synonyms and trade names for methanol are included in Table 1.

This document develops proposed soil and groundwater remediation guidelines consistent with the Alberta Environment Tier I Soil and Groundwater (AENV, 2009a) framework.

2. BACKGROUND INFORMATION

2.1 Chemical and Physical Properties

Chemical and physical properties of methanol are summarized in Table 2. Methanol is characterized as a colourless, polar organic solvent that is miscible with water.

2.2 Analytical Methods

One of the principal reference sources for analytical methods for water, soils, and other materials is the U.S. EPA Document SW-846: "*Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods*" (U.S. EPA, 2004b). U.S. EPA Methods referred to below are sourced from this document. Most techniques for the analysis of methanol in soil include the following three elements:

1. sample extraction;
2. sample preparation; and,
3. separation, followed by detection and quantification of the volatile compounds.

Methanol is first extracted from soil samples using water or another appropriate solvent. This step is not necessary for water samples.

U.S. EPA Methods for Sample Preparation
U.S. EPA-recommended methods for introducing a methanol-containing sample into the GC are summarized below.

- Direct Injection.

- U.S. EPA Method 5031 "Volatile, non-purgeable, water-soluble compounds by azeotropic distillation" involves using an azeotrope with water to introduce the sample into the GC, and is used for water-soluble compounds that are not amenable to purge-and-trap or headspace techniques.

U.S. EPA Methods for Separation and Detection/Quantification
U.S. EPA-recommended methods for methanol for separation and detection/quantification include the following:

- EPA Method 8015B "Non-halogenated organics using GC/FID" provides details of a methodology involving gas chromatographic separation and flame ionization (FID) detector.

- EPA Method 8260B "Volatile organic compounds by gas chromatography/mass spectrometry" provides details of a methodology involving gas chromatographic separation and identification/quantitation using mass spectrometry.

2.3 Production and Uses

The vast majority of commercial methanol is made from synthesis gas. Syngas is produced by steam reforming of methane, LPG or naphtha to produce a mixture of H_2, CO, CO_2, and water. In steam reforming of natural gas, methane and steam are combined in a reactor with a catalyst (Ni) at a temperature between 700 and 1,100°C and at 10 to 50 bar pressure. Methanol is made from purified syngas in tubular reactors packed with catalyst (typically Cu/ZnO on alumina). The overall reaction is $CO + 2H_2 \leftrightarrow CH_3OH$. Methanol synthesis reactors operate at temperatures between 250 and 350°C and at pressures of 30-100 bar (Kirk-Othmer, 1999).

Current capacity for methanol production is 1,370 million gallons (approximately 5 million m^3) per year in the U.S. (9 facilities), and 425 million gallons (approximately 1.6 million m^3) per year in Canada (2 facilities) (ICIS, 2002).

Methanol usage is summarized in Figure 1 (1985 data from a U.S. survey; data source WHO, 1997). As shown in that figure, the majority of methanol production (71%) is used as a chemical feedstock in the synthesis of other industrial chemicals including formaldehyde, acetic acid, methyl halides, and methyl t-butyl ether (MTBE). Other uses of methanol can be categorized into solvent (10%), fuel (6%), and miscellaneous (13%).

Oilfield uses of methanol include hydrate inhibition in natural gas production and transport, removal of acid gasses, as a dehydration agent, in the recovery of heavy hydrocarbons (Esteban et al., 2001), and in the pressure testing of pipelines and pressure vessels in cold temperatures. All of these uses would fall under the "solvent" or "miscellaneous" categories in Figure 1.

2.4 Sources and Emissions

Methanol occurs naturally in humans, animals, and plants. It is a natural constituent of blood, urine, saliva and expired air, and has also been found in mother's milk. Humans have a background body burden of 0.5 mg/kg body weight. Natural emission sources of methanol include volcanic gasses, vegetation, microbes, and insects (WHO, 1997).

Given the high production volume, widespread use and physical and chemical properties of methanol, there is a very high potential for methanol to be released to the environment, principally to air (U.S. EPA, 1976). Emissions of methanol primarily occur from miscellaneous solvent usage, methanol production, end-product manufacturing, and bulk storage and handling losses. The largest source of emissions of methanol is the miscellaneous solvent use category.

In an oilfield setting, emissions of methanol can occur through handling and storage of methanol, leakage from equipment that uses methanol (*e.g.*, wellhead equipment for methanol injection for hydrate suppression), or through the failure of pipelines or pressure vessels undergoing hydrostatic testing with a methanol solution.

2.5 Distribution in the Environment

Methanol can be present in air, water, and soil, both naturally, and as a result of anthropogenic activities. In addition, methanol is present naturally in some foods. Methanol can also be present in consumer products.

Levels in Air

Levels of methanol in air well away from urban centers are generally low. Cavanaugh et al. (1969) reported the methanol concentration in arctic air at Point Barrow, Alaska to be in the range 0.65-1.8 $\mu g/m^3$. The mean methanol concentration at two remote Arizona locations was 3 $\mu g/m^3$ (Snider and Dawson, 1985). Concentrations in urban air are higher, and reported ranges include:

- 10.5-131 $\mu g/m^3$ (Graedel et al., 1986);
- 10 $\mu g/m^3$ (Tucson, Arizona, USA; Snider and Dawson, 1985);
- 5-30 $\mu g/m^3$ (Stockholm, Sweden; Jonsson et al., 1985);
- 0.59-94 $\mu g/m^3$ (dense traffic sites in Stockholm, Sweden; Jonsson et al., 1985);
- 6-60 $\mu g/m^3$ (52 samples from Boston, Houston, and Lima, Ohio, USA; U.S. EPA, 1993)

Methanol has been identified in exhausts from both gasoline and diesel engines and in tobacco smoke (WHO, 1997).

Levels in Soil and Water

In Alberta, methanol spills and releases have been reported to Alberta Environment at concentrations up to 20,000 mg/kg in soil.

Methanol was detected in the USA at a mean level of 0.022 mg/L in rainwater collected during a thunderstorm in Arizona in 1982 (Snider and Dawson, 1985). Methanol at levels of 17-80 mg/L (17-80 ppm) was detected in wastewater effluents from a specialty chemicals manufacturing facility in Massachusetts, USA, but none was detected in associated river water or sediments (Jungclaus et al., 1978). A concentration of 42.4 mg/L was found in a leachate from the Love Canal in Niagara Falls, New York (Venkataraman et al., 1984). Methanol at a level of 1,050 mg/L was detected in condensate waters discharged from a coal gasification plant in North Dakota, USA (Mohr and King, 1985).

Levels in Food

Dietary methanol can arise in large part from fresh fruits and vegetables where it occurs as the free alcohol, methyl esters of fatty acids or the methoxy group on polysaccharides such as pectin. Reported values of the methanol content of fresh and canned fruit juices varies considerably and may range from 1-640 mg/L with an average of 140 mg/L (WHO, 1997)

Methanol was found at levels of 6-27 mg/L in beer, 96-321 mg/L in wines, and 10-220 mg/L in distilled spirits (Greizerstein, 1981). Fermented distilled beverages can contain high levels of methanol, with some spirits having as much as 1,500 mg/L (Francot and Geoffroy, 1956). The methanol content in bourbon was reported to be 40-55 mg/L (Majchrowicz and Mendelson, 1971). The presence of methanol in distilled spirits is directly linked to the pectin content of the raw materials. During the process of making fruit spirits, pectic substances contained in different parts of the fruit undergo degradation by pectin methylases, which can lead to the formation of significant quantities of methanol (Bindler et al., 1988).

Humans can also ingest varying amounts of methanol in foods and or drugs isolated or recrystallized from methanol. Methanol is used as an extraction solvent for spice oleoresins and hops (Lewis, 1989). Additionally, certain foods and drugs, consumed or administered as their methyl ester, can release methanol during their metabolism and excretion. For example, 10% of the sweetening agent aspartame (L-aspartyl-L- phenylalanine methyl ester) hydrolyzes in the gastrointestinal tract to become free methanol. Carbonated beverages contain about 555 mg aspartame/L (WHO, 1997), equivalent to approximately 56 mg methanol per L. However, the amount of methanol present in an average serving of beverage sweetened by aspartame alone is considerably less than in the same volume of many fruit and vegetable juices. For instance, tomato juice will result in 6 times the amount of methanol exposure than consumption of an equivalent volume of aspartame sweetened beverage (Wucherpfennig et al., 1983).

Occurrence in Consumer Products

Methanol is a constituent of a large number of commercially available solvents and consumer products including paints, shellacs, varnishes, paint thinners, cleansing solutions, antifreeze solutions, automotive windshield washer fluids and deicers, duplicating fluids, denaturant for ethanol, and in hobby and craft adhesives. Potentially uses of large quantities of methanol are in its direct use as a fuel, in gasoline blends or as a gasoline extender. Methanol has been identified in exhausts from both gasoline and diesel engines and in tobacco smoke.

2.6 Human Exposure

Methanol occurs naturally in humans, animals, and plants. It is a natural constituent in blood, urine, saliva, and expired air. A mean blood methanol level of 0.73 mg/L in unexposed

individuals (Sedivec et al., 1981) and a range of 0.06 to 0.32 mg/m^3 in expired air (Eriksen and Kulkarni, 1963) have been reported.

The two most important sources of background body burdens for methanol and formate are diet and metabolic processes. Methanol is available in the diet principally from fresh fruits and vegetables, fruit juices, fermented beverages, and diet foods (principally soft drinks). U.S. EPA, (1977) suggest that the average intake of methanol from natural sources would be considerably less than 10 mg methanol/day. However, consumption of a moderate amount of fruit juices and/or aspartame-containing beverages would significantly increase this amount. If aspartame were used to replace all sucrose in the diet, its average daily ingestion would be 7.5-8.5 mg/kg which would be the equivalent to 0.75-0.85 mg methanol/kg (WHO, 1997).

Exposures to methanol can occur in occupational settings through inhalation or dermal contact. Many national occupational health exposure limits suggest that workers are protected from any adverse effects if exposures do not exceed a time-weighted average of 260 mg/m^3 (200 ppm) methanol for any 8-h day and for a 40-h working week. Current general population exposures through air are typically 10,000 times lower than occupational limits. The general population is exposed to methanol in air at concentrations ranging from less than 0.001 mg/m^3 in rural air to nearly 0.04 mg/m^3 in urban air (WHO, 1997).

If the projected use of methanol as an alternate fuel or in admixture with fuels increases significantly, it can be expected that there will be a widespread increase in the exposure of the general population to methanol via inhalation of vapours from methanol-fuelled vehicles and/or siphoning or percutaneous absorption of methanol fuels or blends (WHO, 1997).

Based on the above information, it is clear that for a member of the general population, the primary source of methanol intake is via food. It is also clear that the daily intake of methanol will vary significantly with dietary choices, and will depend strongly on the consumption of fruit and fruit juices, as well as on consumption of the sweetener aspartame. Replacing all sugar in the diet could potentially result in an exposure to methanol several times the tolerable daily intake (TDI).

The guidelines in this document require a value for estimated daily intake (EDI) which is defined at the total dose of a chemical to which an average person is exposed in the absence of any sources of contaminant. The EDI for some individuals may exceed the TDI. Where the EDI exceeds the TDI it is not possible to calculate certain guideline values since the acceptable dose for the chemical is already exceeded by the background exposure. For the purposes of setting guidelines for methanol, the EDI was set at 80% of the TDI, or 0.4 mg/kg bw per day. The rationale for this is that for a person receiving a methanol exposure through food of 80% or more

of the TDI an additional 20% of the TDI is unlikely to have a significant incremental effect. Thus, the EDI used in this report is 0.4 mg/kg bw per day.

Methanol is not reported to be present in uncontaminated soil and accordingly the background soil concentration (BSC) is assumed to be zero.

The concentration of methanol in ambient air is assumed to be 0.04 mg/m^3 based on the WHO value for urban air reported above.

2.7 Existing Criteria, Guidelines and Standards

Canadian Federal

No soil or water quality guidelines for methanol are included in CCME (1999 and updates). Health Canada (2007) does not include methanol in its "Guidelines for Canadian Drinking Water Quality", and does not publish a Tolerable Daily Intake or Tolerable Concentration for methanol (Health Canada, 2004)

Canadian Provincial

Ontario (OMEE, 1994) has set an Interim Provincial Water Quality Objective for methanol of 0.2 mg/L, protective of aquatic life and recreational uses. No other provincial soil or water quality guidelines for methanol were found.

US Federal

The U.S. EPA (2002, 2004a) does not publish a water quality guideline for methanol protective of aquatic life, or a Maximum Contaminant Level (MCL) for methanol in drinking water. Methanol is not included in the list of chemicals for which the U.S. EPA publishes Ecological Soil Screening Levels (EcoSSLs).

US State

No criteria, guidelines, or standards were found for methanol in a limited search of U.S. state information.

Europe

The Dutch Ministry of the Environment (VROM, 2000) have published "Indicative Levels for Serious Contamination" for methanol of 24 mg/L for groundwater and 30 mg/kg for soil. No other European methanol guidelines for soil or groundwater were found.

Australia and New Zealand

Australia and New Zealand have a collaborative set of water quality guidelines protective of aquatic uses (ANZECC, 2000). These guidelines do not include values for methanol. No Australian drinking water guideline has been set for methanol (NHMRC, 1996).

Global

The World Health Organization (WHO, 2004) does not include methanol in its "Guidelines for Drinking Water Quality, Third Edition".

Occupational Exposure Limit

Many jurisdictions have published occupational health exposure limits. WHO (1997) indicate that workers are unlikely to experience any adverse effects if exposures do not exceed a time-weighted average of 260 mg/m^3 (200 ppm) methanol for any 8-h day and for a 40-h working week.

3. ENVIRONMENTAL FATE AND BEHAVIOUR

3.1 Adsorption and Mobility

Methanol has negative log octanol-water (log K_{ow}) and log organic carbon-water (log K_{oc}) partition coefficients (-0.73 and -0.57, respectively, Table 2). Accordingly, sorption of methanol to organic carbon in soil will be minor, and methanol will tend to remain in soil pore water. The mobility of methanol in the subsurface will not be significantly limited by adsorption.

3.2 Aqueous-Phase Solubility

Methanol is miscible with water (Table 2). Accordingly, its mobility in the subsurface will not be limited by solubility.

3.3 Leaching and Lateral Movement

As noted in the two Sections above, the movement of methanol in the subsurface will not be limited by either adsorption or solubility. Consequently, leaching and lateral movement will be potentially significant factors in the subsurface transport of methanol. The hydrogeological retardation factor is the ratio of the rate at which groundwater moves divided by the rate at which a given contaminant in groundwater can be expected to move. If standard (CCME, 2006) properties for coarse and fine soils are assumed, then retardation factors of 1.006 and 1.004 can be calculated for coarse and fine soils, respectively, indicating that the movement of methanol will not be significantly retarded relative to groundwater movement.

API (1994), confirmed the lack of methanol retardation in an aquifer study where an introduced methanol plume was found to move at the same rate as a chloride plume.

3.4 Biodegradation

Methanol has been shown to degrade rapidly under favourable conditions by a number of researchers (Table 3). However, in real environmental settings, degradation can be much slower than in laboratory microcosms due to factors including limited supplies of oxygen and/or other terminal electron acceptors, limited availability of nutrients, and lower temperatures. Thus, degradation rates from field studies typically have more environmental relevance than many laboratory microcosm studies.

Definitive Groundwater Study

One field study was available which gave information relevant to determining a degradation rate for methanol in groundwater. API (1994) injected gasoline, methyl tertiary butyl ether (MTBE)

and methanol in to the shallow sand aquifer at the Borden Site in Ontario. Solute movement and remaining mass were monitored for a period of 500 days via an extensive series of multi-level samplers. Removal of methanol from the aquifer was complete after 400 days. The initial total mass of methanol measured in the aquifer was approximately 14 kg. The total mass was reduced to 7 kg after approximately 245 days, and therefore 245 days is taken as an approximation of the half-life of methanol in groundwater (Table 3). This degradation rate was adopted for guideline development in this document (Table 2). Aquifer conditions in the injection zone prior to the experiment indicated a low background dissolved oxygen of approximately 2 mg/L. Measurements taken during the experiment indicated that initial methanol biodegradation was aerobic. Once oxygen was depleted in the plume, degradation proceeded by anaerobic pathways.

Other Degradation Studies and Data

Howard et al. (1991) quote the half-life of methanol in soil, groundwater, and surface water as being in the range 1-7 days (Table 3).

Methanol has been shown to degrade relatively rapidly in aerobic and anaerobic sludge systems. Available data have been summarized by Verschueren (2001) and are reproduced in Table 3. Figure 2 offers a graphical representation of the methanol degradation data, and shows that in the majority of tests, 50-100% of the methanol in a test system is biodegraded within 5-20 days. However, biodegradation data from aerobic sludges may have little relevance in predicting the biodegradation of methanol in soil and groundwater.

No data were available for methanol biodegradation in soils at natural moisture contents, but low concentrations of methanol (0.1 mg/L) in a soil water suspension were shown to degrade by 53% in 5 days under aerobic conditions, and only slightly less (46%) under anaerobic conditions (Table 3).

A concentration of 800 mg/L methanol was found to halve the oxidation of ammonia by *Nitrosomas* bacteria (*i.e.*, the 50% inhibition concentration, or IC_{50} was 800 mg/L). However, bacterial oxygen consumption was much more robust, with an IC_{50} of 72,000 – 80,000 mg/L (Table 3).

The above data demonstrate that methanol will degrade rapidly in the presence of appropriate bacterial cultures and excess oxygen or other electron acceptors. Thus it may reasonably be anticipated that methanol will degrade rapidly in aerobic surface water or surficial soils. However, groundwater conditions can be very different, and in particular electron acceptors may be limited.

3.5 Volatilization

Volatilization potential is commonly expressed using the vapor pressure and the Henry's law constant of a compound. The Henry's law constant is the equilibrium ratio of the partial pressure in the gas phase to the concentration in the aqueous phase. This value is closely related to the vapour pressure of the pure compound but is also dependent on its aqueous solubility and molecular weight and, therefore, can be used to make a more accurate prediction of volatility than one based on solely on vapour pressure.

Lyman et al. (1982) used Henry's law constants to classify volatilization potential as follows:

- values less than 10^{-7} atm.m^3/mol indicate that the substance is less volatile than water and can be considered essentially non-volatile;
- values between 10^{-7} and 10^{-5} atm.m^3/mol indicate that the substance may volatilize slowly but the compound will still tend to partition into the aqueous phase;
- values between 10^{-5} and 10^{-3} atm.m^3/mol indicate that volatilization is significant; and,
- values greater than 10^{-3} atm.m^3/mol indicate that the majority of the mass of the compound will tend to partition into the gas phase.

The Henry's law constant of methanol is 4.6×10^{-6} atm.m^3/mol (Table 2). Accordingly, by the above definition, methanol may volatilize slowly from an aqueous solution, but will still tend to partition into the aqueous phase.

3.6 Photolysis

No information was available on the atmospheric photolysis or photodegradation of methanol.

4. BEHAVIOUR AND EFFECTS IN TERRESTRIAL BIOTA

4.1 Terrestrial Plants

Seven studies were found that investigated the toxicity of methanol to seven species of terrestrial plants: common onion *(Allium cepa),* lettuce *(Lactuca sativa),* common camellia *(Camellia japonica),* cotton *(Gossypium hirsutum),* potato *(Solanum tuberosum),* soybean *(Glycine max), and* wild carrot *(Daucus carota)* (Table 4). However, none of these studies was conducted using soil as a medium, but rather used plants grown in water or on agar plates, or applied methanol directly to specific plant organs or cells. As such, none of these data are relevant for developing soil remediation guidelines.

Accordingly, definitive (14 or 21 day) growth tests were commissioned (Stantec, 2006) for three plant species, alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*), and northern wheatgrass (*Elymus lanceolatus*). Environment Canada toxicity test protocols (or the most recent available Environment Canada draft protocol, as appropriate) were used for this work with minor modifications to minimize the volatile losses of methanol (Stantec, 2006). A full report on these tests is available at www.ptac.org, and the results are summarized in Table 4. EC25 values for various endpoints for these three species ranged from 1,808 mg/kg to 12,202 mg/kg.

4.2 Soil Invertebrates

No studies on the toxicity of methanol to terrestrial invertebrates in soil were found. However, one study was found on the toxicity of methanol to soil invertebrates in other media. In a 48 hour filter paper test with methanol and *Eisenia fetida*, the LC_{50} was found to be >1,000 $\mu g/cm^2$ (Table 5). This study was not conducted in soil and is not relevant for developing soil quality guidelines.

Reproduction tests were commissioned (Stantec, 2006) for two invertebrate species, the earthworm *Eisenia andrei*, and the springtail *Folsomia canadida.* Environment Canada toxicity test protocols (or the most recent available Environment Canada draft protocol, as appropriate) were used for this work with minor modifications to minimize the volatile losses of methanol (Stantec, 2006). A full report on these tests is available at www.ptac.org, and the results are summarized in Table 5. EC25 values for reproduction endpoints for these two invertebrates ranged from 2,842 mg/kg to 13,323 mg/kg.

4.3 Soil Microbial Processes

No information was available that directly considered the effect of methanol on soil microbial processes. However, information on the degradation of methanol presented in Section 2.3.4.

indicates that bacterial ammonia oxidation in sludge by *Nitrosomas* bacteria is inhibited (IC_{50}) in sludge at 800 mg/L, and the IC_{50} for bacterial oxygen consumption in sludge has been reported to be in the range 72,000 to 80,000 mg/L.

5. BEHAVIOUR AND EFFECTS IN AQUATIC BIOTA

5.1 Freshwater Biota

Toxicological data for freshwater aquatic life for methanol were compiled from the U.S. EPA ECOTOX database (U.S. EPA, 2007b) and other sources, and are summarized in Table 6. A total of 155 data points concerning the toxicity of methanol to freshwater aquatic life were identified. Selected papers were obtained and reviewed in detail as noted in Section 10.2. The studies have undergone classification into primary, secondary, or unacceptable/unverified categories with respect to CCME protocol. 83 of the data points were classified as either primary or secondary data quality.

Effects data from all data quality categories are illustrated in Figure 3, where acute data are shown by hollow diamonds and chronic data by solid diamonds. The freshwater aquatic life toxicological database for methanol is extensive. In general, based on effects concentration ranges illustrated in Figure 3, it appears that fish are more sensitive to methanol than either invertebrates, plants/alga, or other biota. Other biota includes all organisms not in the plant or animal kingdoms.

5.1.1 Freshwater Aquatic Vertebrates

Aquatic toxicity data for freshwater vertebrates in Table 6 include 11 primary and 26 secondary data points from 15 studies that considered 9 species [goldfish *(Carassius auratus),* carp *(Cyprinus carpio),* green sunfish *(Lepomis cyanellus),* bluegill *(Lepomis macrochirus),* carp *(Leuciscus idus melanotus),* rainbow trout *(Oncorhynchus mykiss),* medaka *(Oryzias latipes),* fathead minnow *(Pimephales promelas),* and creek chub *(Semotilus atromaculatus*)]. Effects endpoints for primary and secondary data range from 8 - 29,700 mg/L. Data points showing effects at less than 100 mg/L included the following:

- 8 mg/L for a series of acute tests looking at endocrine disruption and organ weight in rainbow trout (Thorpe et al., 2001);
- 20 mg/L for a chronic test looking at condition in rainbow trout (Harris et al., 2001);
- 40 mg/L for an avoidance test with green sunfish (Summerfelt and Lewis, 1967); and,
- $\leq$ 79 mg/L in a test looking at endocrine disruption (Panter et al., 2002).

The lowest of the LC_{50} data was 1,400 mg/L for a 48 hour test with medaka.

The unacceptable/unverified dataset included 32 data points with effects endpoints ranging from 8 mg/L to 52,000 mg/L.

5.1.2 Freshwater Aquatic Invertebrates

Aquatic toxicity data for freshwater invertebrates in Table 6 include 3 primary and 18 secondary data points from 14 studies that considered 7 species [mussel *(Anodonta imbecillis),* water flea *(Chydorus ovalis, Daphnia magna, Moina macrocopa),* scud *(Hyalella azteca),* oligochaete, worm *(Lumbriculus variegates),* and fairy shrimp *(Streptocephalus proboscideus),*]. Effects endpoints for primary and secondary data range from 37 – 79,100 mg/L. Data points showing effects at less than 100 mg/L include the following:

- 37 mg/L for an acute lethality test in the mussel *Anodonta imbecillis* (Keller, 1993).

The unacceptable/unverified dataset included 13 data points with effects endpoints ranging from 10,000 mg/L to 21,911 mg/L.

5.1.3 Freshwater Aquatic Plants and Algae

Toxicity data for aquatic plants and algae in Table 6 include no primary and 12 secondary data points from 8 studies that considered 6 green algae *(Chlorella fusca vacuolata, Chlorella vulgaris, Chlorella zofingiensis, Chlorococcales, Scenedesmus quadricauda, Selenastrum capricornutum).* Effects endpoints for primary and secondary data range from 791 – 8,000 mg/L.

The unacceptable/unverified dataset included 11 data points with effects endpoints ranging from 80 mg/L to 28,476 mg/L.

5.1.4 Other Freshwater Aquatic Biota

Aquatic toxicity data for other aquatic biota in Table 6 include no primary and 13 secondary data points from 12 studies that considered 8 species [rotifer *(Brachionus calyciflorus),* cryptomonad *(Chilomonas paramecium),* flagellate euglenoid *(Entosiphon sulcatum),* blue-green algae *(Microcystis aeruginosa, and Nostoc sp.),* bryozoan *(Pectinatella gelatinosa),* protozoa *(Spirostomum ambiguum),* and ciliate *(Tetrahymena pyriformis)*]. Effects endpoints for primary and secondary data range from 37 – 79,100 mg/L.

The unacceptable/unverified dataset included 16 data points with effects endpoints ranging from 80 mg/L to 48,060 mg/L.

5.2 Marine Biota

Toxicological data for marine aquatic life for methanol are provided (Table 7). A total of 51 data points were identified. The papers reporting these data have not been reviewed in detail. The studies have undergone preliminary classification into primary, secondary, or unacceptable/unverified categories with respect to CCME protocol. However, it is likely, that some data classified as secondary or unacceptable would be upgraded based on a review of the original paper.

Marine toxicity data are included in this literature search for completeness, but are not directly relevant to developing soil quality guidelines in Alberta and are not discussed further.

6. BEHAVIOUR AND EFFECTS IN HUMANS AND MAMMALIAN SPECIES

There is a large body of data concerning the mammalian toxicity of methanol. Drivers for research in recent years have included: i) the possibility of methanol being increasingly used as a automotive fuel, and the associated increase in inhalation exposure for the general population; and, ii) the observation that aspartame, a widely-used artificial sweetener is hydrolyzed in the human gut to yield methanol.

Health Canada (2004) has not reviewed the toxicity of methanol, or developed a tolerable daily intake or tolerable concentration for methanol. The United States Environmental Protection Agency (U.S. EPA, 2007a) has developed an oral reference dose for methanol, but not an inhalation reference concentration.

The following reviews of the mammalian toxicology of methanol were consulted:

- *Environmental Health Criteria 196—Methanol. World Health Organization. (WHO, 1997).*
- *The toxicity of inhaled methanol vapors. In: Critical Reviews in Toxicology. (Kavet and Nauss, 1990).*
- *NTP-CERHR Expert Panel report on the reproductive and developmental toxicity of methanol. (NTP-CERHR, 2004).*
- *U.S. EPA IRIS database for Risk Assessment – Methanol. U.S. EPA (2007a).*

No attempt is made here to include all the available toxicological data on methanol, but rather the critical elements of methanol toxicity are discussed below, and the key studies are provided in Table 8. Effect and no-effect levels for selected mammalian toxicological studies on methanol are provided in Figure 4, where circles show human data, diamonds show acute animal data, and triangles show chronic animal data. Hollow symbols indicate no effect levels and solid symbols indicate effects.

6.1 Absorption, Metabolism, and Excretion

Methanol is absorbed rapidly following oral, inhalation, or dermal exposure and distributes readily and uniformly to all organs and tissues in direct relation to their water content (Yant and Schrenk, 1937). Thus, all exposure routes are presumed to be toxicologically equivalent (Tephly and McMartin, 1984). No differences exist between the capabilities for absorption of methanol among various animal species, and blood levels are entirely predictable based on the concept that methanol distributes uniformly to body water content (WHO, 1997).

After uptake and distribution, most of the methanol is metabolized in the liver to carbon dioxide (96.9%), while a small fraction is excreted directly to the urine (0.6%) and through the lung. In all mammalian species studied, methanol is metabolized in the liver by sequential oxidative steps to form formaldehyde, formic acid (formate), and CO_2. However, there are profound differences in the rate of formate oxidation in different species which determine the relative sensitivity to methanol (Palese and Tephly, 1975; Eells et al., 1981, 1983). The metabolism of formate is critical in the acute toxicity of methanol, and is discussed further in that section.

The primary route of methanol elimination from the body is via oxidation to formaldehyde and then to formic acid, which may be excreted in the urine or further oxidized to carbon dioxide (WHO, 1997).

6.2 Acute Toxicity

As noted in the above section, formate is an important intermediate metabolite in the eventual metabolic oxidation of methanol to CO_2. Acute methanol toxicity in humans and primates results when the production of formate from the metabolism of methanol is occurring at a greater rate than the formate can be metabolized (WHO, 1997).

In cases of human methanol poisoning, the minimum lethal dose is in the range 0.3 to 1 g/kg (NTP-CERHR, 2004; filled orange circles in Figure 4). Studies with non-human primates have typically yielded lethal doses in the range of 3,000-7,000 mg/kg bw (Table 8). Clinical symptoms observed in primates are similar to those observed in human cases of methanol poisoning, and include initial CNS depression, followed by an asymptomatic latent period of a few hours to two days, followed by acidosis (as a result of the build-up of formic acid in the blood) ocular toxicity, coma and death (WHO, 1997). The mechanism of toxicity in non-primates (including laboratory rodents, rabbits, dogs) is distinct from that in primates in that these species appear to have the ability to metabolize formate more rapidly, and do not develop the acidosis seen in primates. Accordingly, lethal doses reported for non-primates are typically higher those in primates. Examples of the range of lethal dose seen in non-primate species include: 6,000-13,000 mg/kg bw (rat); 7,300-10,000 mg/kg bw (mouse); 7,000 mg/kg bw (rabbit); and 8,000 mg/kg bw (dog) (Table 8, Figure 4).

Acute toxicity to humans from inhalation of methanol vapours follows a very similar clinical pattern to that observed for oral exposure (Kavet and Nauss, 1990).

6.3 Subchronic and Chronic Toxicity

Only limited studies are available on the longer-term toxicity of methanol (Figure 4), other than the reproductive, developmental, and carcinogenicity studies discussed below.

The U.S. EPA reviewed the database of longer-term oral studies for methanol, and deemed that none were a suitable basis for the development of an oral RfD. Accordingly, the U.S. EPA commissioned a sub-chronic oral study on the toxicity of methanol to rats (U.S. EPA, 1986). Sprague-Dawley rats were gavaged daily with 0, 100, 500, or 2,500 mg/kg bw/day of methanol for 90 days. At the highest dose, effects were noted on liver function, as evidenced by elevated levels of SGPT, SAP, and increased, but not statistically significant, liver weights in both male and female rats. Elevated levels of the enzymes SGTP and SAP in blood are indicators of liver damage. These data suggest possible treatment-related effects in rats dosed with 2,500 mg methanol/kg bw/day despite the absence of supportive histopathologic lesions in the liver. Accordingly, the NOEL and LOAEL for this study were set at 500 and 2,500 mg/kg bw/day, respectively.

The Japanese New Energy Development Organization (NEDO) has conducted longer-term inhalation studies on rats, mice, and monkeys. Rats and mice were exposed to methanol vapours for 12 months; no effects were seen at 100 ppm, but slight effects on weight gain (decreased in rats, increased in mice) were seen in both species at 1,000 ppm which is the LOEC for this study (NEDO, 1987, Katoh, 1989). In an earlier study (NEDO, 1982), no effects were found on monkeys exposed to 1,000 ppm methanol for 29 months.

6.4 Carcinogenicity and Genetic Toxicity

There have been no studies reported in the peer-reviewed literature on the potential carcinogenicity of methanol in either humans or laboratory animals (WHO, 1997). However, unpublished reports from the New Energy Development Organization (NEDO, 1987; Katoh, 1989) in Japan included carcinogenicity studies on mice and rats exposed by inhalation to methanol vapours at up to 1,300 mg/m^3 for up to 24 months. No evidence of carcinogenicity was found in either species. It is unlikely that methanol is carcinogenic to mouse skin. In a dermal exposure study on mice with an exposure period of 50 weeks and observation for lifetime, no indication of methanol-related carcinogenicity was reported (Lijinsky et al., 1991). While the database on carcinogenicity is extremely limited, no evidence suggesting that methanol is carcinogenic to animals or humans was found.

A number of *in-vitro* and *in-vivo* studies have investigated the genetic toxicity of methanol.

Endpoints studied in *in-vitro* tests include:

- incorporation assays with the bacterium *Salmonella typhimurium;*
- DNA repair test in the bacterium *E. coli;*
- chromosomal malsegregation in the fungus *Aspergillus nidulans;*

- gene mutation in the yeast *Schizosaccharomyces pombe;*
- mutagenicity test in the fungus *Neurospora crassa;*
- sister chromatid exchanges in Chinese hamster cells;
- mutation frequency in mouse lymphoma cells;
- cell transformation in Syrian hamster embryo cells; and,
- cell transformation in rat embryo cell.

Results from the *in-vitro* tests were mostly negative, with a few positive results (WHO, 1997).

In-vivo tests have considered a range of genotoxicity endpoints in mice exposed to methanol via oral, inhalation, and intraperitoneal routes. As with the *in-vitro* tests, the majority of the results were negative, but some positive results were obtained (WHO, 1997).

WHO (1997) considers that the structure of methanol (by analogy with ethanol) does not suggest that it would be genotoxic. Overall, the weight of evidence appears to suggest that methanol is likely not genotoxic.

6.5 Reproduction and Developmental Toxicity

NTP-CERHR (2004) reviewed the human and animal toxicological data on the developmental and reproductive toxicity of methanol. They concluded that the human data were insufficient to evaluate either the developmental or the reproductive toxicity of methanol. The developmental toxicity data in rats and mice were judged to be consistent and sufficient to determine that inhalation or oral exposure to methanol is a developmental hazard. Mice were judged to be more sensitive than rats to inhaled methanol. However, the data from primates was deemed insufficient to draw the same conclusions. The methanol database on reproduction in rodents is fragmented and uneven, and currently insufficient to draw a conclusion regarding methanol's effects on female or male reproductive function.

Rogers et al. (1993) is deemed to be a critical developmental study. Mice were exposed to methanol vapour at doses of 1,000, 2,000, 5,000, 7,500, 10,000, or 15,000 ppm for 7 h per day on days 6 to 15 of pregnancy. No fetal effects were seen at 1,000 ppm (fetal NOAEC), but an increase in the frequency of cervical ribs was observed at 2,000 ppm (fetal LOAEC). NTP-CERHR (2004) assessed the maternal NOAEC from this study to be 15,000 ppm.

Rogers et al. (1993) also established dose comparability across inhalation and oral gavage exposure by demonstrating that twice daily gavage with 2,000 mg/kg bw per day methanol on days 6-15 of pregnancy resulted in a blood methanol level and developmental pattern of response similar to that in mice exposed to 10,000 ppm methanol vapour.

Nelson et al. (1985) is another significant developmental study. Rats were exposed to methanol vapour at doses of 5,000, 10,000, or 20,000 ppm for 7 h per day on days 1 to 19 of pregnancy (the top dose group were exposed on day 7-15). No fetal effects were seen at 5,000 ppm (fetal NOAEC), but a decrease in fetal weight was observed at 10,000 ppm (fetal LOAEC). No maternal effects were seen at 10,000 ppm (maternal NOAEC), but unsteady gait was observed during initial exposure to 20,000 ppm (maternal LOAEC).

NTP-CERHR (2004) concluded that developmental toxicity was the most sensitive endpoint of concern with respect to evaluating the risk to reproduction posed by methanol exposure in humans.

The results of these and other key studies are summarized in Table 8.

6.6 Tolerable Daily Intake/Concentration

Health Canada (2004) has not reviewed the toxicity of methanol, or developed a tolerable daily intake or tolerable concentration for methanol. Human exposure limits for methanol used in this document are summarized in Table 9.

The U.S. EPA (2007a) developed an oral reference dose for methanol, but not an inhalation reference concentration. The U.S. EPA (2007a) based their RfD on a sponsored National Toxicology Program (NTP) study (U.S. EPA, 1986), reviewed in Section 6.3, above. The NOEL and LOAEL for this study were 500 and 2,500 mg/kg bw/day, respectively. U.S. EPA (2007a) used this study to develop and oral reference dose (RfD, equivalent to a tolerable daily intake, or TDI) of 0.5 mg/kg bw/day, by applying an uncertainty factor of 1,000 to the NOEL from this study. The uncertainty factor of 1,000 comprised multiplicative factors of 10 for each of: i) interspecies extrapolation from rats to humans; ii) intraspecies variations in the sensitivity of humans; and, iii) extrapolation from sub-chronic to chronic exposure. This value of 0.5 mg/kg bw/day is used as the oral TDI for methanol in this report (Table 9).

No inhalation reference concentration (RfC) or tolerable concentration (TC) for methanol developed by regulatory authorities was found in this literature review. However, methanol is absorbed rapidly via both inhalation and oral exposures (WHO, 1997) and methanol toxicity appears to correlate closely with blood methanol level independent of exposure route (NTP-CERHR, 2004). In addition, Rogers et al. (1993) established dose comparability across inhalation and oral gavage exposure in mice. Accordingly, it is deemed reasonable to extrapolate the U.S. EPA (2007a) oral RfD to estimate a human TC. Using an adult human body weight of 70.7 kg and inhalation rate of 15.8 m^3/day (Table 10), a tolerable concentration for methanol inhalation exposure of 2.2 mg/m^3 was estimated (Table 9). This value was used as the inhalation TC for this report.

7. TOXICITY OF DEGRADATION PRODUCTS

In certain cases, organic compounds can have degradation products that are more toxic than the parent compound. Prudent management of such a parent compound should take into consideration the possibility of more toxic degradation products. A complete review of the toxicity of degradation products is outside the scope of the current study. However, it is worth noting that formaldehyde is a potential degradation product of methanol. Dutch environmental regulators (VROM, 2000), provide "indicative levels for serious contamination" for formaldehyde in soil and groundwater of 0.1 mg/kg and 0.05 mg/L, respectively. These values are 2-3 orders of magnitude lower than the corresponding values for methanol (30 mg/kg and 24 mg/L), indicating that the Dutch regulators consider formaldehyde significantly more toxic than methanol.

Consistent with other guideline development work conducted by AENV and others, no attempt was made to incorporate possible formaldehyde toxicity in the guidelines for methanol. However, formaldehyde should always be analyzed at any site with a significant methanol release, and the results managed on a site-specific basis.

8. DATA ADEQUACY AND DATA GAPS

The available data for methanol were assessed against CCME (2006) and AENV (2009a) requirements for developing soil and water quality guidelines.

8.1 Soil Quality Guidelines

Human Health Guidelines

Sufficient data are available to develop soil quality guidelines protective of human soil ingestion, indoor air inhalation, and potable groundwater, based on CCME (2006) requirements.

Ecological Guidelines

A battery of terrestrial toxicity tests was commissioned for this project and the results form an adequate database for guideline development for the soil eco-contact pathway based on CCME (2006) requirements.

None of the available data are suitable for calculating the nutrient and energy cycling check, and accordingly, this check was not calculated for methanol. A soil quality guideline can be calculated without this check.

Insufficient data exist to calculate the soil and food ingestion guideline. The CCME (2006) protocol for this guideline requires toxicity data from tests conducted on livestock species, and these data do not currently exist.

There are sufficient data to calculate the soil quality guideline protective of groundwater for freshwater aquatic life, based on CCME (2006) requirements.

8.2 Groundwater Quality Guidelines

Drinking Water

Sufficient data are available to develop a "Source Guidance Value for Groundwater" to use as a basis for the development of a soil quality guideline protective of potable groundwater.

Freshwater Aquatic Life

The freshwater aquatic life dataset for methanol is extensive, and sufficient for the development of an interim freshwater aquatic life guideline (CCME, 1991).

Irrigation Water

Insufficient data are available to calculate a water quality guideline for irrigation.

Livestock Watering

Insufficient data are available to meet the CCME (2006) requirements for developing a livestock watering guideline.

9. PARAMETER VALUES

Parameter values required to calculate Alberta Tier 1 soil and groundwater remediation guidelines for methanol fall into two main groups: i) parameters that relate to the chemical properties, toxicity, or background exposure to methanol, referred to as "chemical-specific parameters"; and, ii) parameters relating to receptor exposure and properties of the site, referred to as "non-chemical-specific parameters". These two groups of parameters are discussed below.

9.1 Chemical-Specific Parameters

Chemical-specific parameters for methanol are summarized in Table 9, together with an indication of where to find a discussion of the rationale for the value selected. The soil allocation factor (SAF) and water allocation factor (WF) each take their default values of 0.2, since exposure to methanol is possible via all five potentially contaminated environmental media: soil, water, air, food, and consumer products.

9.2 Non Chemical-Specific Parameters

Non chemical-specific parameter values are taken without change from AENV (2009a). Parameter values for human receptor characteristics, soil and hydrogeological parameters, site characteristics, and building parameters are provided in Tables 10 to 13, respectively.

10. SURFACE WATER GUIDELINES

AENV and the CCME use surface water quality guidelines as a basis from which to calculate corresponding groundwater and soil quality guidelines. Surface water quality guidelines calculated for methanol are provided and discussed below.

10.1 Human Drinking Water

No Canadian Drinking Water Quality Guideline (CDWQG) currently exists for methanol. In such cases, CCME (2006) includes a protocol for calculating an allowable concentration in potable water (Source Guidance Value for Groundwater) from the tolerable daily intake using the following equation:

$$SGVG = \frac{TDI \times BW \times WF}{WIR}$$

where:

SGVG	=	Source Guidance Value for Groundwater (mg/L)
TDI	=	tolerable daily intake (mg/kg/d)
BW	=	body weight (kg)
WF	=	water allocation factor (unitless)
WIR	=	water ingestion rate (L/d)

The SGVG is calculated using adult parameters (CCME, 2006). Substituting appropriate parameter values form Tables 9 and 10 gives a value of 4.7 mg/L which is the Source Guidance Value for Groundwater for methanol. This value is rounded to 1 significant figure with a 5 or 0 in the second figure to give 4.5 mg/L in Table 14, but 2 significant figures are retained for the calculation of soil quality guidelines.

10.2 Freshwater Aquatic Life

An interim freshwater aquatic life water quality guideline for methanol was calculated based on the CCME (1991) protocol. Freshwater aquatic toxicity data were obtained from the U.S. EPA ECOTOX database and other sources, discussed in Section 5.1, and are summarized in Table 6.

10.2.1 Data Quantity Requirements

Insufficient data exist for the development of a full freshwater aquatic life water quality guidelines. However, minimum data requirements are met for the development of an interim

guideline (two acute and/or chronic studies on two or more fish species, including one cold water species resident in North America; two acute and/or chronic studies on two or more invertebrate species from different classes, including one planktonic species).

10.2.2 Ecological Relevance

Guidelines are developed from ecologically relevant data. Accordingly, the toxicity endpoints in Table 6 were screened for ecological relevance. Due to the large number of studies in Table 6, and the fact that the CCME (1991) protocol uses the lowest relevant endpoints, the assessment of ecological relevance was conducted sequentially by acquiring and reviewing papers starting with the lowest reported effect concentration to determine the lowest relevant endpoint. A summary is provided below, in which each study is introduced by its reference, followed by the effect concentration recorded in Table 6, and an indication of whether or not the study is considered relevant to guideline development.

Geyer et al. (1984), (0 mg/L methanol). This was a bioaccumulation study, and included no valid toxicological endpoints. Accordingly, this study was not considered further.

Thorpe et al., (2000), (8 mg/L methanol). This was a 21 day study on the estrogenic properties of 17β-estradiol, 4-*tert*-nonylphenol and methoxychlor on juvenile rainbow trout. Methanol was used as a solvent carrier. Results for the solvent control indicated that at 0.01 ml methanol per litre (8 mg/L), there was no effect on any of the endpoints studied (body weight, K-factor, hepatosomatic indices, gonadosomatic indices, or plasma vitellogenin). Accordingly, this study indicates no adverse effects for methanol and is not considered further.

Thorpe et al., (2001), (8 mg/L methanol). This was a 14 day study on the estrogenic properties of 17β-estradiol, 4-*tert*-nonylphenol and methoxychlor and binary combinations thereof on juvenile rainbow trout. Methanol was used as a solvent carrier. Results for the solvent control indicated that at 0.01 ml methanol per litre (8 mg/L), there was no detectable increase in plasma vitellogenin. Accordingly, this study indicates no adverse effects for methanol and is not considered further.

Harris et al., (2001), (16 mg/L methanol). This was an 18 week study on the estrogenic effects of 4-nonylphenol on adult female rainbow trout, using flow-through vessels. This study is considered chronic, based on the duration relative to the lifespan of the trout. The species is native to Canadian rivers and therefore relevant. Methanol was used as a solvent carrier in the experiment. Results for the solvent control indicated that at 0.002% methanol (16 mg/L), there was no significant change, relative to the dilution water control, in length, body weight, K-factor, hepatosomatic indices, gonadosomatic indices, or pituitary gland gonadotrophin levels. Statistically significant decreases in plasma 17β-estradiol were seen at 6 and 12 weeks but not at

0 or 18 weeks. Statistically significant increases in plasma GTH-1 (a gonadotrophin) level were seen at 12 and 18 weeks but not at 0 or 6 weeks. Due to the lack of a consistent response in these parameters in plasma, the lack of a corresponding effect in the pituitary gonadotrophin, and the lack of any affect on the gonadosomatic indices, it is questionable whether these results are ecologically, or merely statistically significant. However, given the potential ecological impact of endocrine disruptors, the precautionary principle was applied and the results from this study were deemed to be relevant for guideline development.

Thus the lowest ecologically relevant chronic toxicity endpoint is 16 mg/L which is a LOEC for changes in the levels of two hormones in adult female rainbow trout in an 18 week study.

Keller (1993) (37 mg/L methanol). This was a 48 hour mortality test on the unionid mussel *Anodonta imbecilis*. The reported LC50 for methanol was 37 mg/L. Controls were conducted and deemed satisfactory in the U.S. EPA ECOTOX review. This result is considered relevant for guideline development since unionid mussels are native to Canada, the endpoint (mortality) is ecologically relevant, and the study quality appears to be acceptable. Considering that the lifespan of unionid mussels can be many years, a 48 hour test would be considered an acute exposure.

Thus the lowest ecologically relevant acute toxicity endpoint is 37 mg/L which is the 48 hour LC50 for *Anodonta imbecilis*.

10.2.3 Guideline Development

The CCME (1991) protocol for calculating the guideline considers primary and secondary data and takes the lower of:

1. the lowest LOEC for a chronic study for a non-lethal endpoint is multiplied by a safety factor of 0.1.
2. The lowest EC50 or LC50 for an acute test is multiplied by an application factor of 0.05 (methanol is considered non-persistent in surface water based on a half life of 1 to 7 days, Table 3).

Chronic Studies

As noted above, the lowest endpoint from a chronic study among the primary and secondary data in Table 6 is 16 mg/L which is a LOEC for changes in the levels of two hormones in adult female rainbow trout in an 18 week study. Therefore, a freshwater aquatic life water quality guideline based on a chronic study is calculated by multiplying the LOEC of 16 mg/L from this study by a safety factor of 0.1 to give a guideline value of 1.6 mg/L.

Acute Studies

The freshwater guideline derived from the lowest relevant acute EC50/LC50 is calculated by multiplying the Keller (1993) 48 hour LC50 for *Anodonta imbecilis* by an application factor of 0.05 to give a guideline value of 1.9 mg/L.

The guidelines derived from the lowest chronic and acute studies give a consistent result. However, the guideline from the chronic study is the lower of the two, and accordingly, the freshwater aquatic life water quality guideline for methanol is 1.6 mg/L. This value is rounded to 1 significant figure with a 5 or 0 in the second figure to give 1.5 mg/L in Table 14, but 2 significant figures are retained for the calculation of soil or groundwater quality guidelines.

10.3 Irrigation Water

No guideline was calculated for methanol in irrigation water, since the minimum data requirements were not met. Due to the volatility and ready degradability of methanol in surface water and shallow aerobic soil systems, this exposure pathway is not expected to be an issue at the majority of sites.

10.4 Livestock and Wildlife Watering

Methanol toxicity data were not available for livestock or wildlife species, and accordingly, these guidelines could not be calculated.

11. SOIL AND GROUNDWATER GUIDELINE CALCULATIONS – HUMAN HEALTH

11.1 Direct Contact

The model used to calculate the soil quality guideline protective of the human direct soil contact (soil ingestion, dermal contact, and particulate inhalation) exposure pathway for methanol is taken without change from AENV (2009a). Based on guidance in AENV (2009a), exposure via particulate inhalation is not considered for volatile compounds such as methanol, since volatile chemicals are presumed to be lost from soil particles during wind transport. Excluding the particulate inhalation pathway was achieved by setting IR_s to 0 kg/day for volatile chemicals in the equations below. Parameter values are summarized in Tables 9 and 10. The following equation was used.

$$PSQG_{HH} = \frac{(TDI - EDI) \times SAF \times BW}{\left[(AF_G \times SIR) + (AF_L \times IR_S \times ET_2) + (AF_S \times SR)\right] \times ET_1} + [BSC]$$

Where:

$PSQG_{HH}$	=	preliminary human health-based soil quality guideline (mg/kg)
TDI	=	tolerable daily intake (mg/kg bw per day)
EDI	=	estimated daily intake (mg/kg bw per day)
SAF	=	soil allocation factor (dimensionless)
BW	=	adult or toddler body weight (kg)
AF_G	=	absorption factor for gut (dimensionless)
AF_L	=	absorption factor for lung (dimensionless)
AF_S	=	absorption factor for skin (dimensionless)
SIR	=	adult or toddler soil ingestion rate (kg/day)
IR_S	=	inhalation of particulate matter re-suspended from soil (kg/day)
SR	=	adult or toddler soil dermal contact rate, see below (kg/day)
ET_1	=	exposure term 1 (dimensionless) (days/week ÷ 7 x weeks/year ÷ 52)
ET_2	=	exposure term 2 (dimensionless) (hours/day ÷ 24)
BSC	=	background soil concentration (mg/kg)

Substituting appropriate values from Tables 9 and 10 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of 2,000 mg/kg (agricultural and residential), 3,500 mg/kg (commercial), and 16,000 mg/kg (industrial) for the human direct contact guideline (Tables 15 and 16).

Soil Dermal Contact Rate

The soil dermal contact rate (SR) is the mass of contaminated soil which is assumed to contact the skin each day. This parameter is calculated as follows (AENV, 2009a):

$$SR = \{(SA_H \times DL_H) + (SA_O \times DL_O)\} \times EF$$

Where:

SR	=	soil dermal contact rate (kg/day)
SA_H	=	exposed surface area of hands (m^2)
DL_H	=	dermal loading of soil to hands (kg/m^2 per event)
SA_O	=	area of exposed body surfaces other than hands (m^2)
DL_O	=	dermal loading of soil to other surfaces (kg/m^2 per event)
EF	=	exposure frequency (events/day)

The soil dermal contact rate is calculated separately for toddlers and adults using the parameters in Table 10.

11.2 Inhalation

Soil and groundwater guidelines protective of the indoor infiltration and inhalation pathway were calculated using the equations from AENV (2009a) without change for soil and groundwater.

11.2.1 Model Assumptions

Assumptions implicit in the model include the following:

- contaminant vapour immediately above the groundwater table is assumed to be in equilibrium with contaminant concentrations in the groundwater based on Henry's Law;
- the soil is physically and chemically homogeneous;
- cracks in the building floor slab are filled with dry material of the underlying soil type,
- the moisture content is uniform throughout the unsaturated zone;
- decay of the contaminant source is not considered (*i.e.*, infinite source mass);
- attenuation of the contaminant in the unsaturated zone is not considered; and,
- interactions of the contaminant with other chemicals or soil minerals are not considered.

11.2.2 Soil

The equation used was as follows (AENV, 2009a).

$$SQG_I = \frac{(TC - C_a) \times [\theta_w + (K_{oc} \times f_{oc} \times \rho_b) + (H' \times \theta_a)] \times SAF \times DF_i \times 10^3}{H' \times \rho_b \times ET \times 10^6} + BSC$$

Where:

SQG_I	=	soil quality guideline for indoor infiltration (mg/kg)
TC	=	tolerable concentration (mg/m^3)
C_a	=	background air concentration (mg/m^3)
θ_w	=	moisture-filled porosity (dimensionless)
K_{oc}	=	organic carbon partition coefficient (L/kg)
f_{oc}	=	fraction of organic carbon (g/g)
ρ_b	=	dry soil bulk density (g/cm^3)
H'	=	dimensionless Henry's Law Constant (dimensionless)
θ_a	=	vapour-filled porosity (dimensionless)
SAF	=	soil allocation factor (dimensionless)
DF_i	=	dilution factor from soil gas to indoor air (calculated below)
10^3	=	conversion factor from kg to g
ET	=	exposure term (dimensionless)
10^6	=	conversion factor from m^3 to cm^3
BSC	=	background soil concentration (mg/kg)

Substituting appropriate values from Tables 9, 10, 11, and 13 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of 150 mg/kg (agricultural and residential, coarse soil), 2,000 mg/kg (commercial and industrial, coarse soil), Table 15, and 3,500 mg/kg (agricultural and residential, fine soil), 25,000 mg/kg (commercial and industrial, fine soil), Table 16.

11.2.3 Groundwater

The equation used was as follows (AENV, 2009a).

$$GWQG_I = \frac{(TC - C_a) \times SAF \times DF_i}{H' \times ET \times 10^3}$$

Where:

$GWQG_I$	=	groundwater quality guideline for indoor infiltration (mg/L)
TC	=	tolerable concentration (mg/m^3)
C_a	=	background air concentration (mg/m^3)
SAF	=	soil allocation factor (dimensionless)
DF_i	=	dilution factor from soil gas to indoor air (calculated below)
H'	=	dimensionless Henry's Law Constant (dimensionless)
ET	=	exposure term (dimensionless)
10^3	=	conversion factor from m^3 to L

Substituting appropriate values from Tables 9, 10, 11, and 13 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of 2,000 mg/L (agricultural

and residential, coarse soil), 30,000 mg/L (commercial and industrial, coarse soil), 30,000 mg/L (agricultural and residential, fine soil), and 200,000 mg/L (commercial and industrial, fine soil) (Table 17).

11.2.4 Dilution Factor Calculation

This section presents the (AENV, 2009a) equations that were used to calculate the dilution factor in the above equations. The dilution factor (DF_i) was calculated as follows:

$$DF_i = \frac{1}{\alpha}$$

Where: DF_i = dilution factor from soil gas concentration to indoor air concentration (unitless)

α = attenuation coefficient (unitless; see derivation below).

Calculation of α

The attenuation coefficient, α, was calculated using the following equation:

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right) exp\left(\frac{Q_{soil} L_{crack}}{D_{crack} A_{crack}}\right)}{exp\left(\frac{Q_{soil} L_{crack}}{D_{crack} A_{crack}}\right) + \left(\frac{D_T^{eff} A_B}{Q_B L_T}\right) + \left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right)\left[exp\left(\frac{Q_{soil} L_{crack}}{D_{crack} A_{crack}}\right) - 1\right]}$$

where:

α = attenuation coefficient (dimensionless)

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)

A_B = building area (cm^2)

Q_B = building ventilation rate (cm^3/s)

L_T = distance from contaminant source to foundation (cm)

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)

L_{crack} = thickness of the foundation (cm)

D_{crack} = effective vapour diffusion coefficient through the crack (cm^2/s)

A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2)

Calculation of D_T^{eff}:

$$D_T^{eff} \approx D_a \times \left(\frac{\theta_a^{10/3}}{\theta_t^2} \right)$$

Where: D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = diffusion coefficient in air (cm^2/s)
θ_a = soil vapour-filled porosity (dimensionless)
θ_t = soil total porosity (dimensionless)

Calculation of D_{crack}:

D_{crack} is calculated in exactly the same way as D_T^{eff}, with the exception that the assumption is made that the soil material in the cracks is dry (AENV, 2009a), and accordingly, the air filled porosity is the same as the total porosity, and the equation becomes:

$$D_{crack} \approx D_a \times \left(\frac{\theta_t^{10/3}}{\theta_t^2} \right)$$

Where: D_{crack} = effective porous media diffusion coefficient in floor cracks (cm^2/s)
D_a = diffusion coefficient in air (cm^2/s)
θ_t = total porosity for coarse soil (dimensionless)

Calculation of Q_B:

$$Q_B = \frac{L_B W_B H_B ACH}{3{,}600}$$

Where: Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm)
W_B = building width (cm)
H_B = building height (cm)
ACH = air exchanges per hour (h^{-1})
3,600 = conversion factor from hours to seconds

Calculation of Q_{soil}:

$$Q_{soil} = \frac{2\pi\Delta P k_v X_{crack}}{\mu \, ln\left[\frac{2Z_{crack}}{r_{crack}}\right]}$$

Where Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm \cdot s^2$)
k_v = soil vapour permeability to vapour flow (cm^2)
X_{crack} = length of idealized cylinder (cm)
μ = vapour viscosity (0.000173 g/cm·s)
Z_{crack} = distance below grade to idealized cylinder (cm)
r_{crack} = radius of idealized cylinder (cm; calculated as A_{crack}/X_{crack})

11.3 Offsite Migration

"Offsite Migration" guidelines are calculated to check that the guideline set for commercial and industrial land use will not result in adjacent more sensitive land being contaminated at levels above the applicable guideline for the sensitive land due to wind and/or water transport of contaminated soil from the commercial or industrial site. However, the guideline is not applicable to volatile or readily degradable compounds (CCME, 2006) since significant contaminant mass loss is expected to occur during wind and/or water transport of contaminated soil.

Accordingly, the soil quality guideline protective of off-site migration is not calculated for methanol.

12. ECOLOGICAL EXPOSURE PATHWAYS

12.1 Direct Contact

12.1.1 Soil

The soil quality guideline for the exposure pathway considering direct contact of plants and soil invertebrates (the "eco-contact pathway") is calculated based on a weight of evidence approach following CCME (2006). Data relevant for guideline development are sourced from Stantec (2006) (available at www.ptac.org) and are summarized in Tables 4 and 5. The values provided in Tables 4 and 5 are nominal values based on the known amount of chemical spiked into the test soils. Stantec (2006) included analytical data to confirm exposure concentrations. The regression for the analytical data was $y = 0.9714x - 401.66$ where x is the nominal concentration and y the measured concentration. The CCME (2006) protocol uses data standardized at the 25th percentile effect level. EC25 data, corrected for analytical recovery, are summarized below.

Species	Endpoint	EC25 (mg/kg)
Alfalfa	Shoot Length	1,748
Alfalfa	Root Length	7,317
Alfalfa	Shoot Dry Mass	1,355
Alfalfa	Root Dry Mass	2,716
Barley	Shoot Length	4,344
Barley	Root Length	5,186
Barley	Shoot Dry Mass	2,064
Barley	Root Dry Mass	2,341
Northern Wheatgrass	Shoot Length	3,629
Northern Wheatgrass	Root Length	11,452
Northern Wheatgrass	Shoot Dry Mass	2,393
Northern Wheatgrass	Root Dry Mass	3,129
Eisenia andrei	Number of Progeny	12,540
Eisenia andrei	Dry Mass of Individual Progeny	9,076
Folsomia candida	Number of Progeny	2,359

The 25th percentile of these data is the eco-contact guideline for natural areas, agricultural and residential. The 50th percentile of these data is the eco-contact guideline for commercial and industrial land use. The eco-contact guidelines for methanol are summarized below (rounded to 1 significant figure with a 5 or a 0 as the second figure) and included in Tables 15 and 16.

- 25th percentile - natural areas, agricultural and residential eco-contact guideline: 2,500 mg/kg
- 50th percentile - commercial and industrial land use eco-contact guideline: 3,000 mg/kg

12.1.2 Groundwater

The direct contact of shallow groundwater with plants and soil invertebrates exposure pathway is applicable whenever groundwater is present within 3 m of the ground surface. However, based on guidance in AENV (2009a), the guideline is not calculated for polar compounds such as methanol. The rationale for this position is that the potential interactions between polar organic compounds and soils are complex in that they can be highly dependant on various environmental conditions including pH, clay mineralogy, and redox conditions. Attempting to set groundwater guidelines for polar chemicals for this pathway would involve significant uncertainty, and accordingly, it is recommended that concerns with potential adverse effects on surface soil biota from polar organic compounds in shallow groundwater be addressed on a site-specific basis by analyzing soil samples.

Accordingly, the groundwater guideline protective of the eco-contact pathway is not calculated for methanol.

12.2 Nutrient and Energy Cycling

Insufficient data were available and this guideline was not calculated for methanol.

12.3 Soil and Food Ingestion

Insufficient data were available (Section 8.1), and this guideline was not calculated for methanol. However, this exposure pathway was not expected to be a concern, since i) methanol is expected to degrade rapidly in surficial soil (Table 3) and accordingly livestock and wildlife are unlikely to get significant exposure to methanol through incidental ingestion of surficial soil; and ii) based on its very low K_{ow} (Table 2) methanol is not expected to accumulate into plants to any significant extent, and thus the exposure of livestock or wildlife to methanol in soil is expected to be minimal.

12.4 Offsite Migration

"Offsite Migration" guidelines are calculated to check that the guideline set for commercial and industrial land use will not result in adjacent more sensitive land being contaminated at levels above the applicable guideline for the sensitive land due to wind and/or water transport of contaminated soil from the commercial or industrial site. However, the guideline is not applicable to volatile or readily degradable compounds (CCME, 2006) since significant contaminant mass loss is expected to occur during wind and/or water transport of contaminated soil.

Accordingly, the soil quality guideline protective of off-site migration is not calculated for methanol.

13. GROUNDWATER PATHWAYS

This section provides the protocols used to calculate soil and groundwater remediation objectives protective of exposure pathways involving groundwater. The following receptors are considered:

- humans (potable drinking water sourced from groundwater); and,
- aquatic life (via lateral groundwater transport and discharge into a surface water body).

In the first case, it is assumed that a water well could potentially be installed at any location, and hence it is assumed that there is no lateral offset between the location where the contaminated soil or groundwater is measured and the receptor.

In the second case, a minimum lateral separation of 10 m is assumed between the location where the contaminated soil or groundwater is measured and the location of the surface water body. In cases where contamination is present within 10 m of a surface water body, a site-specific approach will be required (see AENV, 2009b).

Surface water quality guidelines protective of the above water uses are provided in Table 14.

13.1 Soil Remediation Guidelines

Soil remediation guidelines for groundwater pathways were calculated using the model and equations from AENV (2009a)

13.1.1 Model Assumptions

Assumptions implicit in the model include the following:

- the soil is physically and chemically homogeneous;
- moisture content is uniform throughout the unsaturated zone;
- infiltration rate is uniform throughout the unsaturated zone;
- decay of the contaminant source is not considered (*i.e.*, infinite source mass);
- contaminant is not present as a free phase product;
- maximum possible concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions;
- the groundwater aquifer is unconfined;
- groundwater flow is uniform and steady;
- co-solubility and oxidation/reduction effects are not considered;

- attenuation of the contaminant in the saturated zone is assumed to be one dimensional with respect to sorption-desorption, dispersion, and biological degradation;
- dispersion in groundwater is assumed to occur in the longitudinal and transverse directions only and diffusion is not considered;
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes; and
- dilution of the plume by groundwater recharge down-gradient of the source is not considered.

13.1.2 Guideline Calculation

The soil remediation guideline protective of groundwater uses is calculated in the same way for both groundwater uses noted at the start of this section, using the corresponding surface water quality guideline (Table 14) as the starting point for each. However, as noted above, the lateral offset between the point at which the contaminated soil is measured and the surface water body (parameter "x" in the equation for DF4 below) is assumed to be 10 m for aquatic life, and 0 m for human drinking water.

The model considers four processes:

1. partitioning from soil to leachate;
2. transport of leachate from base of contamination to water table;
3. mixing of leachate and groundwater; and,
4. groundwater transport down-gradient to a discharge point.

For each of these four processes, a dilution factor was calculated (DF1 through DF4, respectively). DF1 has units of (mg/kg)/(mg/L) or L/kg. The other three dilution factors are dimensionless [units of (mg/L)/(mg/L)]. The overall dilution factor is used to calculate the soil concentration that is protective of groundwater using the following equations:

$$SQG_{GR} = SWQG \times DF$$

$$DF = DF1 \times DF2 \times DF3 \times DF4$$

where:

SQG_{GR}	=	soil quality guideline protective of groundwater pathways (mg/kg)
SWQG	=	corresponding surface water quality guideline (drinking water or aquatic life) (mg/L)
DF	=	overall dilution factor (L/kg)
DF1	=	dilution factor for process 1 (L/kg)
DF2	=	dilution factor for process 2 (dimensionless)

DF3 = dilution factor for process 3 (dimensionless)
DF4 = dilution factor for process 4 (dimensionless)

Dilution Factor 1

Dilution factor 1 (DF1) is the ratio of the concentration of a contaminant in soil to the concentration in leachate that is in contact with the soil. This "dilution factor" represents the three phase partitioning between contaminant sorbed to soil, contaminant dissolved in pore water (*i.e.*, as leachate), and contaminant present as soil vapour. DF1 is calculated using the following equation:

$$DF1 = K_{oc} \times f_{oc} + \frac{(\theta_w + H' \times \theta_a)}{\rho_b}$$

where:

DF1 = dilution factor 1 (L/kg)
K_{oc} = organic carbon-water partition coefficient (L/kg)
f_{oc} = fraction organic carbon (g/g)
θ_w = water filled porosity (dimensionless)
H' = dimensionless Henry's Law constant (dimensionless)
θ_a = air filled porosity (dimensionless)
ρ_b = dry soil bulk density (g/cm^3)

Dilution Factor 2

Dilution factor 2 (DF2) is the ratio of the concentration of a contaminant in leachate that is in contact with the soil, to the concentration in pore water just above the groundwater table. DF2 takes the value 1.00 (*i.e.,* no dilution) for generic guidelines because it is assumed at Tier 1 that the contaminated soil extends down to the water table. DF2 can be calculated on a site-specific basis at Tier 2.

Dilution Factor 3

Dilution factor 3 (DF3) is the ratio of the concentration of a chemical in pore water just above the groundwater table, to the concentration in groundwater beneath the source. This dilution factor reflects a decrease in concentration as leachate mixes with uncontaminated groundwater. DF3 is a function of groundwater velocity, infiltration rate, source length, and mixing zone thickness. The mixing zone thickness is calculated as being due to two processes: i) mixing due to dispersion, and ii) mixing due to infiltration rate. The equations used are as follows:

$$DF3 = 1 + \frac{Z_d \times V}{I \times X}$$

$$Z_d = r + s$$

$$r = 0.01 \times X$$

$$s = d_a \left\{ 1 - exp\left(\frac{-2.178 \times X \times I}{V \times d_a} \right) \right\}$$

$$V = K \times i$$

where:

DF3	=	dilution factor 3 (dimensionless)
Z_d	=	average thickness of mixing zone (m)
V	=	Darcy velocity in groundwater (m/year)
I	=	infiltration rate (m/year)
X	=	length of contaminated soil (m)
r	=	mixing depth due to dispersion (m)
s	=	mixing depth due to infiltration rate (m)
d_a	=	unconfined aquifer thickness (m)
K	=	aquifer hydraulic conductivity (m/year)
i	=	lateral hydraulic gradient in aquifer (dimensionless)

Note that the parameter Z_d takes the fixed value of 2 m for the drinking water pathway, but is calculated for all other pathways.

Dilution Factor 4

Dilution factor 4 (DF4) accounts for the processes of dispersion and biodegradation as groundwater travels downgradient from beneath the source of contamination, and is the ratio of the concentration of a chemical in groundwater beneath the source, to the concentration in groundwater at a distance of 10 m (at Tier 1 for aquatic life) downgradient of the source. Consistent with AENV (2009a), the time independent version of the equation to calculate DF4 was used:

$$DF4 = \frac{2}{\exp(A) \times [erf(C) - erf(D)]}$$

$$A = \frac{x}{2D_x} \left\{ 1 - \left(1 + \frac{4L_s D_x}{v} \right)^{1/2} \right\}$$

$$C = \frac{y + Y/2}{2(D_y x)^{1/2}}$$

$$D = \frac{y - Y/2}{2(D_y x)^{1/2}}$$

$$L_s = \frac{0.6931}{t_{1/2s}} \times \exp(-0.07d)$$

$$v = \frac{V}{\theta_t R_s}$$

$$R_s = 1 + \frac{\rho_b K_{oc} f_{oc}}{\theta_t}$$

$$D_x = 0.1x$$

$$D_y = 0.01x$$

where:

DF4	=	dilution factor 4 (dimensionless)
erf	=	the error function
A	=	dimensionless group A (dimensionless)
C	=	dimensionless group C (dimensionless)
D	=	dimensionless group D (dimensionless)
x	=	distance to source (10 m, aquatic life and wildlife watering, 0 m other water uses)
D_x	=	dispersivity in the direction of groundwater flow (m)
L_s	=	decay constant (1/year)
v	=	velocity of the contaminant (m/year)
y	=	distance to receptor perpendicular to groundwater flow (m)
Y	=	source width (m)
D_y	=	dispersivity perpendicular to the direction of groundwater flow (m)
$t_{1/2s}$	=	decay half-life of contaminant in saturated zone of aquifer (years)
d	=	water table depth (m)
V	=	Darcy velocity in groundwater (m/year)
θ_t	=	total soil porosity (dimensionless)
R_s	=	retardation factor in saturated zone (dimensionless)
ρ_b	=	dry soil bulk density (g/cm^3)
K_{oc}	=	organic carbon partition coefficient (mL/g)

f_{oc} = fraction organic carbon (g/g)

Aquatic Life

Substituting appropriate values from Tables 9, 10, 11, and 12 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of 0.75 mg/kg for coarse soil (Table 15), and 20 mg/kg for fine soil (Table 16).

Protection of Domestic Use Aquifer

Substituting appropriate values from Tables 9, 10, 11, and 12 into this equation, setting x to 0, and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of 9.0 mg/kg for coarse soil (Table 15), and 10.0 mg/kg for fine soil (Table 16).

13.2 Groundwater Remediation Guidelines

Groundwater remediation guidelines for groundwater pathways were calculated using the model and equations from AENV (2009a).

13.2.1 Potable Groundwater

If contaminated groundwater is considered a domestic use aquifer, there is no offset assumed between contamination and a potential future water well, and therefore the Source Guidance Value for Groundwater (4.7 mg/L, rounded to 4.5 mg/L) applies directly to groundwater (Table 17).

13.2.2 Aquatic Life

Assumptions implicit in the model include the following:

- the soil/aquifer material in the saturated zone is physically and chemically homogeneous;
- decay of the contaminant source is not considered (*i.e.*, infinite source mass);
- the contaminant is not present as a free phase product;
- groundwater flow is uniform and steady;
- co-solubility and oxidation/reduction effects are not considered;
- dispersion is assumed to occur in the longitudinal and transverse directions only and diffusion is not considered; and,
- dilution of the plume by groundwater recharge down-gradient of the source is not considered.

Guideline Calculation

The groundwater remediation guideline protective of aquatic life is calculated using the following equations.

$$GWQG_{GR} = SWQG \times DF4$$

where: $GWQG_{GR}$= groundwater quality guideline protective of aquatic life (mg/L)
$SWQG_{FL}$= surface water quality guideline protective of aquatic life (mg/L)
DF4 = dilution factor for process 4 (L/kg)

Dilution factor 4 is calculated in the same way as described in Section 13.1.2

Substituting appropriate values from Tables 9, 10, 11, and 12 into the above equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of 2 mg/L for coarse soil, and 45 mg/L for fine soil (Table 17).

14. MANAGEMENT LIMIT

Management limits are soil guidelines values that take into consideration issues beyond direct human or ecological toxicity. This includes issues such as aesthetics (odour, soil appearance), flammability, and risk of infrastructure damage. No information was available on methanol concentrations that would lead to offensive odours or to infrastructure damage. However, data were available on the flammability of soils containing methanol, and a management limit was calculated for methanol based on flammability.

A series of experiments were conducted by Methanex, a major worldwide producer of methanol, on the flammability of field soil samples contaminated with methanol (Terry Rowat, Methanex Corporation, *pers. comm.*). A trench was dug outward from an area of known high methanol contamination towards an area without methanol contamination. The soil in this area was a clay till. The trench provided access to soils with a range of methanol concentrations depending on the point along the trench from which the sample was taken. A series of samples was collected, and a sub-sample from each sample was preserved for analysis at the Methanex Kitimat lab. Then an attempt was made to ignite each sample, and an observation made as to whether the sample would burn. The results from these experiments are provided in Table 18, and indicate that the lowest concentration of methanol which would support combustion was 9,310 mg/kg. Samples at 7,460 mg/kg and lower did not support combustion.

A safety factor of 10 was used together with the concentration of 7,460 mg/kg noted above to set the value for the flammability check for methanol in soil to 750 mg/kg (rounded to 1 significant figure with a 5 or a 0 in the second figure, Tables 15 and 16).

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TABLES

Table 1. Common Synonyms and Trade Names for Methanol

Trade Names and Synonyms	
Methanol	Methyl alcohol
Carbinol	colonial spirit
columbian spirit	columbian spirits
Methanol	Methanol
methyl hydroxide	Methylol
monohydroxymethane	pyroxylic spirit
Wood alcohol	wood naphtha
wood spirit;	

Table 2. Physical and Chemical Properties for Methanol

Property	Units	Methanol	Source
Formula	-----	CH_3OH	1
CAS number	-----	67-56-1	1
Molecular weight	g/mole	32.04	2
Melting point	°C	-97.8	2
Boiling point	°C	64.7	2
Specific gravity (at 20/4 °C)	g/cm^3	0.791	2
Vapour density (air = 1)	-----	1.11	3
Vapour pressure (at 5 °C)	Pa	5,320	3,7
Vapour pressure (at205 °C)	Pa	12,236	2
Solubility (at 25 °C)	mg/L	miscible	2
	g/L	1,163	3
Henry's law constant	$atm \cdot m^3/mol$	4.6×10^{-6}	3
Dimensionless Henry's law constant	-----	2.0×10^{-4}	5
Organic carbon partition coefficient (K_{oc})	log	-0.57	4
n-Octanol-water partition coefficient (K_{ow})	log	-0.73	3
	log	-0.66	2
Diffusion coefficient in air	cm^2/s	0.15	11
Conversion factor: 1ppm =	mg/m^3	1.31	8
Odour threshold (unadapted panelists)	mg/m^3	2,660	9
Biodegration half-life in soil	days	1 to 7	6
Biodegration half-life in surface water	days	1 to 7	6
Biodegration half-life in groundwater	days	245	10

Sources:

[1]CRC (1996)

[2]Werl Treatability Database (1993) as reported in GRI (1996)

[3]Montgomery (1991)

[4]Calculated from K_{ow} using Baker et al. (1997) equation provided in Boethling and Mackay (2000; Table 8.1)

[5]Recalculated using the ideal gas law

[6]Howard et al. (1991)

[7]Recalculated from Montgomery (1991; 40 mm Hg) using the conversion 1 mm Hg = 1 torr = 133 Pa

[8]Adapted from Clayton and Clayton (1982)

[9]Verschueren (2001)

[10]Derived From API (1994), see text

[11]Oak Ridge National Laboratory (2007)

Table 3. Summary of Available Information on Methanol Biodegradation

Test Method	Test Duration	Initial Compound Concentration	% Removed	Inoculum or Medium	Rates / Comments	Reference
Definitive Groundwater Study						
Aquifer Study	500 days	7,034	100%	groundwater	half-life = 245 days (see Section 3.4)	API (1994)
Other Data						
NV	NV	NV	NV	soil	half life in soil: 1-7 days	Howard et al. (1991)
NV	NV	NV	NV	groundwater	half life in groundwater 1-7 days	Howard et al. (1991)
NV	NV	NV	NV	surface water	half life in surface water 1-7 days	Howard et al. (1991)
BOD_5	5 days	NV	48%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	NV	53%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	NV	75%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	NV	69%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	500-1,500 mg/L	9%	10% sewage	ThOD	Verschueren (2001)
BOD_5	5 days	1-1,000 mg/L	40-73%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	NV	51-57%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	NV	51%	sewage	ThOD	Verschueren (2001)
BOD_5	5 days	NV	75%	sewage	ThOD	Verschueren (2001)
BOD_5	5 days	NV	83%	sewage	ThOD	Verschueren (2001)
BOD_5	5 days	6,000 mg/L	83%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	6,000 mg/L	96%	NV	ThOD	Verschueren (2001)
BOD_5	5 days	NV	62%	NV	ThOD; aclimated	Verschueren (2001)
BOD_5	5 days	10 mg/L	75%	unadapted sewage	ThOD; lag period = 1 day	Verschueren (2001)
BOD_{10}	10 days	2.5 mg/L	63%	sewage	ThOD	Verschueren (2001)
BOD_{10}	10 days	NV	63%	NV	ThOD	Verschueren (2001)
BOD_{10}	10 days	NV	88%	NV	ThOD	Verschueren (2001)
BOD_{10}	10 days	NV	84%	NV	ThOD	Verschueren (2001)
BOD_{15}	15 days	NV	69%	NV	ThOD	Verschueren (2001)
BOD_{15}	15 days	NV	91%	NV	ThOD	Verschueren (2001)
BOD_{15}	15 days	NV	85%	NV	ThOD	Verschueren (2001)

Table 3. Summary of Available Information on Methanol Biodegradation

Test Method	Test Duration	Initial Compound Concentration	% Removed	Inoculum or Medium	Rates / Comments	Reference
BOD_{20}	20 days	NV	67%	NV	ThOD	Verschueren (2001)
BOD_{20}	20 days	NV	95%	NV	ThOD	Verschueren (2001)
BOD_{20}	20 days	NV	97%	NV	ThOD	Verschueren (2001)
BOD_{20}	20 days	NV	84%	NV	ThOD	Verschueren (2001)
BOD_{20}	20 days	NV	79%	unadapted sewage	ThOD; lag period = 1 day	Verschueren (2001)
BOD_{30}	30 days	NV	69%	NV	ThOD	Verschueren (2001)
BOD_{40}	40 days	NV	93%	NV	ThOD	Verschueren (2001)
BOD_{50}	50 days	NV	98%	NV	ThOD	Verschueren (2001)
aerobic	5 days	0.1 mg/L	53%	soil-water suspension	mineralization to CO_2	Verschueren (2001)
anaerobic	5 days	0.1 mg/L	46%	soil-water suspension	mineralization to CO_2	Verschueren (2001)
ammonium oxidation inhibition test	NV	800 mg/L	NV	sludge digestion by *Nitrosomas*	IC_{50} for oxidation of NH_3	Verschueren (2001)
oxygen consumption inhibition test	NV	72,000 mg/L	NV	municipal sludge	IC_{50} for oxygen consumption	Verschueren (2001)
oxygen consumption inhibition test	NV	80,000 mg/L	NV	industrial sludge	IC_{50} for oxygen consumption	Verschueren (2001)
respiration inhibition test	3 hour	>1,000 mg/L	NV	activated sludge	IC_{50} for respiration	Verschueren (2001)
bacterial growth inhibition test	16 hour	>5,000 mg/L	NV	sludge digestion by *Nitrosomas*	IC_{50} for oxygen consumption	Verschueren (2001)

[a]Biochemical oxygen demand (BOD) is defined as parts of oxygen consumed per part of compound during degradation. This value is expressed as a percentage of the theoretical (ThOD) oxygen demand.

NV = not reported in the abstract and not verified in this literature search

Table 4. Toxicity of Methanol to Terrestrial Plants

Scientific Name	Common Name	Effect Measurement	Concentration	Endpoint/ Response	Response Site	Test Duration	Media Type	Application Method	Chemical Analysis	Reference
						days				
Data Relevant for Guideline Development										
Medicago sativa	Alfalfa	Length	2,213	EC25	shoot	14	artificial soil	spiked	Y	Stantec (2006)
Medicago sativa	Alfalfa	Length	7,945	EC25	root	14	artificial soil	spiked	Y	Stantec (2006)
Medicago sativa	Alfalfa	Dry Mass	1,808	EC25	shoot	14	artificial soil	spiked	Y	Stantec (2006)
Medicago sativa	Alfalfa	Dry Mass	3,209	EC25	root	14	artificial soil	spiked	Y	Stantec (2006)
Hordeum vulgare	Barley	Length	4,886	EC25	shoot	14	artificial soil	spiked	Y	Stantec (2006)
Hordeum vulgare	Barley	Length	5,752	EC25	root	14	artificial soil	spiked	Y	Stantec (2006)
Hordeum vulgare	Barley	Dry Mass	2,538	EC25	shoot	14	artificial soil	spiked	Y	Stantec (2006)
Hordeum vulgare	Barley	Dry Mass	2,823	EC25	root	14	artificial soil	spiked	Y	Stantec (2006)
Elymus lanceolatus	Northern Wheatgrass	Length	4,149	EC25	shoot	21	artificial soil	spiked	Y	Stantec (2006)
Elymus lanceolatus	Northern Wheatgrass	Length	12,202	EC25	root	21	artificial soil	spiked	Y	Stantec (2006)
Elymus lanceolatus	Northern Wheatgrass	Dry Mass	2,877	EC25	shoot	21	artificial soil	spiked	Y	Stantec (2006)
Elymus lanceolatus	Northern Wheatgrass	Dry Mass	3,635	EC25	root	21	artificial soil	spiked	Y	Stantec (2006)
Data Not Relevant for Guideline Development										
Allium cepa	Common onion	Growth	19,300 mg/L	EC50	NR	6	aqueous	NR	NV	Fiskesjo (1985)
Lactuca sativa	Lettuce	Germination	40,850 mg/L	EC50	NR	3	agar	NR	NV	Reynolds (1977)
Gossypium hirsutum	Cotton	Damage	25 uL	no change compared to control	fruit	0.21	culture medium	injection	NV	Guinn (1977)
Gossypium hirsutum	Cotton	ethylene	26 uL	50% of control	fruit	0.21	culture medium	injection	NV	Guinn (1977)
Solanum tuberosum	Potato	Damage	32,040 mg/L	no change compared to control	cell	0.01	NR	soaked	NV	Stiles and Stirk (1931)
Solanum tuberosum	Potato	Damage	64,080 mg/L	no change compared to control	cell	0.01	NR	soaked	NV	Stiles and Stirk (1931)
Glycine max	Soybean	Biomass	1,922 mg/L	50% of control	shoot	4.08	NR	soaked	NV	Eisenmenger (1930)

Table 4. Toxicity of Methanol to Terrestrial Plants

Scientific Name	Common Name	Effect Measurement	Concentration	Endpoint/ Response	Response Site	Test Duration	Media Type	Application Method	Chemical Analysis	Reference
						days				
Glycine max	Soybean	Biomass	10,000 mg/L	49% of control	cell	11	culture medium	soaked	NV	Davis et al. (1978)
Glycine max	Soybean	Biomass	20,000 mg/L	82% of control	cell	11	culture medium	soaked	NV	Davis et al. (1978)
Glycine max	Soybean	Biomass	5,000 mg/L	13% of control	cell	11	culture medium	soaked	NV	Davis et al. (1978)
Glycine max	Soybean	Size	1,922 mg/L	18% of control	root	4.08	NR	soaked	NV	Eisenmenger (1930)
Daucus carota	Wild carrot	Biomass	20,000 mg/L	20% of control	cell	14	culture medium	soaked	NV	Davis et al. (1978)
Daucus carota	Wild carrot	Biomass	10,000 mg/L	27% of control	cell	7	culture medium	soaked	NV	Davis et al. (1978)
Daucus carota	Wild carrot	Biomass	20,000 mg/L	13% of control	cell	7	culture medium	soaked	NV	Davis et al. (1978)

Notes: NV = not reported in the abstract and not verified in this literature search

Table 5. Toxicity of Methanol to Terrestrial Invertebrates

Scientific Name	Common Name	Effect Measurement	Concentration	Endopint/Response	Test Duration	Media Type	Application Method	Chemical Analysis	Reference
					days				
Data Relevant for Guideline Development									
Eisenia andrei	Earthworm	adult survival	17,199	EC50	35	artificial soil	spiked	Y	Stantec (2006)
Eisenia andrei	Earthworm	# progeny	13,323	EC25	63	artificial soil	spiked	Y	Stantec (2006)
Eisenia andrei	Earthworm	progeny mass	9,756	EC25	63	artificial soil	spiked	Y	Stantec (2006)
Folsomia candida	Springtail	# progeny	2,842	EC25	28	artificial soil	spiked	Y	Stantec (2006)
Data Not Relevant for Guideline Development									
Eisenia fetida	earthworm	Mortality	>1,000 ug/cm^2	LC50	2	filter paper	direct application	NV	Roberts and Dorough (1984)

Notes:

NV = not reported in the abstract and not verified in this literature search

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
Primary Data													
invertebrate	*Daphnia pulex*	water flea	acute	1 mi	79,100	NV	locomotion	static	NV	10	measured	satisfactory	Gannon and Gannon (1975)
invertebrate	*Chydorus ovalis*	water flea	acute	96 h	<=20,000	NV	mortality	renewal	7.04-7.97	23.3	measured	satisfactory	Bailey et al. (1996)
invertebrate	*Chydorus ovalis*	water flea	acute	96 h	>20,000	LC_{50}	mortality	renewal	7.04-7.97	23.3	measured	satisfactory	Bailey et al. (1996)
vertebrate	*Pimephales promelas*	fathead minnow	acute	96 h	29,400	LC_{50}	mortality	flow through	7	27	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	weight	flow through	8	NV	measured	satisfactory	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	acute	48 h	29,700	EC_{50}	lost equilibrium	flow through	NV	NV	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Lepomis macrochirus*	bluegill	acute	96 h	15,400	LC_{50}	mortality	flow through	7.04-7.97	19.8	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	96 h	15,029	LC_{50}	mortality	static	7.04-7.97	19.8	measured	satisfactory	Mayer and Ellersieck (1986)
vertebrate	*Lepomis macrochirus*	bluegill	acute	96 h	12,700	EC_{50}	lost equilibrium	flow through	6.5-8.5	20	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	96 h	13,000	EC_{50}	lost equilibrium	flow through	6.5-8.5	20	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Lepomis macrochirus*	bluegill	acute	96 h	>10,000	LC0	mortality	static	7.4	25	measured	satisfactory	Buzzell et al. (1968)
vertebrate	*Pimephales promelas*	fathead minnow	acute	96 h	28,900	EC_{50}	lost equilibrium	flow through	7	27	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	96 h	20,100	LC_{50}	mortality	flow through	NV	NV	measured	satisfactory	Poirier et al. (1986)
vertebrate	*Pimephales promelas*	fathead minnow	acute	96 h	28,200	LC_{50}	mortality	flow through	NV	NV	measured	satisfactory	Veith et al. (1983)
Secondary Data													
invertebrate	*Lumbriculus variegatus*	oligochaete, worm	acute	96 h	>100	LC_{50}	mortality	static	NV	NV	nominal	satisfactory	Ewell et al. (1986)
invertebrate	*Daphnia pulex*	water flea	acute	24 h	27,468	EC_{50}	immobilization	static	7.9	21	nominal	satisfactory	Lilius et al. (1995)
invertebrate	*Daphnia magna*	water flea	acute	48 h	24,500	EC_{50}	immobilization	static	NV	25	nominal	satisfactory	Randall and Knopp (1980)
invertebrate	*Daphnia obtusa*	water flea	acute	24 h	23,500	EC_{50}	immobilization	static	NV	25	nominal	satisfactory	Rossini and Ronco (1996)
invertebrate	*Streptocephalus proboscideus*	fairy shrimp	acute	24 h	32,640	LC_{50}	mortality	NV	7.7	15	nominal	satisfactory	Calleja et al. (1994)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
invertebrate	*Daphnia magna*	water flea	acute	0.25 h	32,000	NV	locomotion	static	6.9	20	nominal	satisfactory	Anderson (1944)
invertebrate	*Daphnia pulex*	water flea	acute	18 h	19,538	LC_{50}	mortality	static	7.04-7.97	23.3	nominal	satisfactory	Bowman et al. (1981)
invertebrate	*Hyalella azteca*	scud	acute	18 h	19,380	LC_{50}	mortality	static	7.04-7.97	23.3	nominal	satisfactory	Bowman et al. (1981)
invertebrate	*Daphnia magna*	water flea	acute	24 h	4,816	LC_{50}	mortality	NV	6.2-9	25	nominal	satisfactory	Guilhermino et al. (2000)
invertebrate	*Anodonta imbecillis*	mussel	acute	48 h	37	LC_{50}	mortality	static	NV	NV	nominal	satisfactory	Keller (1993)
invertebrate	*Daphnia magna*	water flea	acute	24 h	20,804	EC_{50}	immobilization	static	NV	NV	nominal	satisfactory	Lilius et al. (1994)
invertebrate	*Daphnia magna*	water flea	acute	24 h	21,376	EC_{50}	immobilization	NV	NV	NV	nominal	satisfactory	Calleja et al. (1994)
invertebrate	*Daphnia obtusa*	water flea	acute	48 h	22,200	EC_{50}	immobilization	static	NV	NV	nominal	satisfactory	Rossini and Ronco (1996)
invertebrate	*Streptocephalus proboscideus*	fairy shrimp	acute	24 h	32,640	LC_{50}	mortality	static	NV	NV	nominal	satisfactory	Calleja and Persoone (1992)
invertebrate	*Daphnia pulex*	water flea	acute	3 h	48,000	LC_{50}	mortality	NV	NV	15	NV	satisfactory	Nishiuchi and Hashimoto (1967)
invertebrate	*Moina macrocopa*	water flea	acute	3 h	52,000	LC_{50}	mortality	NV	NV	NV	NV	satisfactory	Nishiuchi and Hashimoto (1967)
invertebrate	*Daphnia magna*	water flea	acute	48 h	3,289	LC_{50}	mortality	NV	6.2-9	25	nominal	satisfactory	Guilhermino et al. (2000)
invertebrate	*Daphnia pulex*	water flea	acute	0.5-1 mi	79,100	NV	locomotion	static	NV	20	nominal	satisfactory	Gannon and Gannon (1975)
other	*Spirostomum ambiguum*	protozoa	acute	24 h	37,391	LC_{50}	mortality	static	7.8	21	nominal	satisfactory	Nalecz-Jawecki and Sawicki (1999)
other	*Chilomonas paramecium*	cryptomonad	NV	NV	441	NV	growth	NV	NV	20	nominal	satisfactory	Bringmann and Kuhn (1981)
other	*Spirostomum ambiguum*	protozoa	acute	24 h	23,485	EC_{50}	deformation	static	NV	25	nominal	satisfactory	Nalecz-Jawecki and Sawicki (1999)
other	*Tetrahymena pyriformis*	ciliate	chronic	48 h	18,756	EC_{50}	growth	static	7.04-7.97	12.7	nominal	satisfactory	Schultz et al. (1990)
other	*Brachionus calyciflorus*	rotifer	acute	24 h	35,840	LC_{50}	mortality	NV	7	20	nominal	satisfactory	Calleja et al. (1994)
other	*Microcystis aeruginosa*	blue-green algae	NV	NV	530	LOEC	growth	static	6.9-7.5	14.9-15.5	nominal	satisfactory	Bringmann and Kuhn (1978b)
other	*Brachionus calyciflorus*	rotifer	acute	24 h	35,840	LC_{50}	mortality	static	NV	22	nominal	satisfactory	Calleja and Persoone (1992)
other	*Tetrahymena pyriformis*	ciliate	acute	1 mi	32,040	NV	immobilization	static	NV	NV	nominal	satisfactory	Noever et al. (1994)
other	*Chilomonas paramecium*	cryptomonad	chronic	48 h	441	NV	growth	NV	NV	20	nominal	satisfactory	Bringmann et al. (1980)
other	*Tetrahymena pyriformis*	ciliate	acute	2 d	18,756	IC_{50}	growth	static	7.04-7.97	12.7	nominal	satisfactory	Schultz and Tichy (1993)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
other	*Entosiphon sulcatum*	flagellate euglenoid	chronic	72 h	10,000	NV	growth	static	6.5	25	nominal	satisfactory	Bringmann and Kuhn (1980a)
other	*Nostoc sp.*	blue-green algae	chronic	10-14 d	54,800	EC_{50}	growth	static	NV	10	nominal	satisfactory	Stratton (1987)
other	*Pectinatella gelatinosa*	bryozoan	acute	0.5-2 h	100000-1000000	NV	reproduction	NV	NV	NV	nominal	satisfactory	Mukai (1977)
plant/alga	*Chlorella vulgaris*	green algae	chronic	4 d	1,582	NV	growth	NV	8.1-8.2	20	nominal	satisfactory	El Jay (1996)
plant/alga	*Scenedesmus quadricauda*	green algae	chronic	8 d	8,000	NV	growth	static	NV	17	nominal	satisfactory	Bringmann and Kuhn (1978c)
plant/alga	*Scenedesmus quadricauda*	green algae	NV	NV	8,000	NV	growth	static	NV	17	nominal	satisfactory	Bringmann and Kuhn (1977a)
plant/alga	*Scenedesmus quadricauda*	green algae	NV	NV	8,000	LOEC	growth	static	NV	22	nominal	satisfactory	Bringmann and Kuhn (1978b)
plant/alga	*Chlorella vulgaris*	green algae	chronic	4 d	791	NV	growth	NV	7.04-7.54	15.2-15.8	nominal	satisfactory	El Jay (1996)
plant/alga	*Selenastrum capricornutum*	green algae	chronic	4 d	791	NV	growth	NV	7.04-7.54	15.2-15.8	nominal	satisfactory	El Jay (1996)
plant/alga	*Chlorella zofingiensis*	green algae	chronic	48 h	801	NOEC	assimilation efficiency	static	7.11-8.42	19.4-21	nominal	satisfactory	Weber et al. (1984)
plant/alga	*Chlorococcales*	green algae order	acute	24 h	1,600	EC10	assimilation efficiency	static	6.2-9	25	nominal	satisfactory	Krebs (1991)
plant/alga	*Chlorella zofingiensis*	green algae	chronic	48 h	3,204	LOEC	assimilation efficiency	static	6.2-9	25	nominal	satisfactory	Weber et al. (1984)
plant/alga	*Chlorella zofingiensis*	green algae	chronic	48 h	7,113	EC_{50}	assimilation efficiency	static	6.2-9	25	nominal	satisfactory	Weber et al. (1984)
plant/alga	*Scenedesmus quadricauda*	green algae	chronic	7 d	8,000	NV	growth	static	7.6	21	nominal	satisfactory	Bringmann and Kuhn (1980a)
plant/alga	*Chlorella fusca vacuolata*	green algae	acute	24 h	0	BCF	accumulation	static	NV	18-May	nominal	satisfactory	Geyer et al. (1984)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	14 d	8	NV	vitellogenin	flow through	NV	20	nominal	satisfactory	Thorpe et al. (2001)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	14 d	8	NV	vitellogenin	flow through	NV	20	nominal	satisfactory	Thorpe et al. (2001)
vertebrate	*Pimephales promelas*	fathead minnow	acute	24 h	29,700	LC_{50}	mortality	flow through	NV	25	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Semotilus atromaculatus*	creek chub	acute	24 h	17,000	LC_{100}	mortality	static	7.04-7.97	12.7	nominal	satisfactory	Gillette et al. (1952)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
vertebrate	*Lepomis macrochirus*	bluegill	acute	48 h	16,000	EC_{50}	lost equilibrium	flow through	7.04-7.97	19.8	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Lepomis macrochirus*	bluegill	acute	24 h	19,100	LC_{50}	mortality	flow through	7.04-7.97	23.3	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Lepomis macrochirus*	bluegill	acute	48 h	19,100	LC_{50}	mortality	flow through	7.04-7.97	23.3	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	24 h	>10,000	LC_{50}	mortality	static	6.9	25	nominal	satisfactory	Tsuji et al. (1986)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	24 h	>10,000	LC_{50}	mortality	static	7.53	25.4	nominal	satisfactory	Tsuji et al. (1986)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	24 h	20,300	LC_{50}	mortality	flow through	NV	NV	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Pimephales promelas*	fathead minnow	acute	24 h	29,700	EC_{50}	lost equilibrium	flow through	NV	NV	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	48 h	20,100	LC_{50}	mortality	flow through	6.9	NV	nominal	satisfactory	Poirier et al. (1986)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	48 h	1,400	LC_{50}	mortality	static	8.1-8.2	20	nominal	satisfactory	Tsuji et al. (1986)
vertebrate	*Lepomis macrochirus*	bluegill	acute	72 h	17,720	LC_{50}	mortality	flow through	7.04-7.97	12.7	nominal	satisfactory	Call et al. (1983)
vertebrate	*Carassius auratus*	goldfish	acute	48 h	2,100	LC_{50}	mortality	NV	6.2-9	25	nominal	satisfactory	Nishiuchi and Hashimoto (1967)
vertebrate	*Leuciscus idus melanotus*	carp	acute	48 h	7,900	LC0	mortality	NV	6.2-9	25	nominal	satisfactory	Juhnke and Luedemann (1978)
vertebrate	*Leuciscus idus melanotus*	carp	acute	48 h	7,900	LC0	mortality	NV	6.2-9	25	nominal	satisfactory	Juhnke and Luedemann (1978)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	0-21 d	8	NV	organ weight	flow through	8.1-8.2	16.3	nominal	satisfactory	Thorpe et al. (2000)
vertebrate	*Cyprinus carpio*	carp	acute	6 h	791	NV	biochemistry	static	7.11-8.42	19.4-21	nominal	satisfactory	Gluth and Hanke (1984)
vertebrate	*Cyprinus carpio*	carp	acute	6 h	791	NV	biochemistry	static	7.11-8.42	19.4-21	nominal	satisfactory	Gluth and Hanke (1984)
vertebrate	*Cyprinus carpio*	carp	acute	6 h	791	NV	physiology	renewal	7.11-8.42	19.4-21	nominal	satisfactory	Gluth and Hanke (1984)
vertebrate	*Cyprinus carpio*	carp	acute	6 h	791	NV	biochemistry	static	7.04-7.54	15.2-15.8	nominal	satisfactory	Gluth and Hanke (1984)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	chronic	6-18 wk	16	NV	condition	flow through	NV	25	nominal	satisfactory	Harris et al. (2001)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	chronic	6-18 wk	16	NV	hormone (estradiol)	flow through	NV	NV	nominal	satisfactory	Harris et al. (2001)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	chronic	6-18 wk	16	NV	hormone (fsh)	flow through	NV	NV	nominal	satisfactory	Harris et al. (2001)
vertebrate	*Lepomis cyanellus*	green sunfish	acute	0.08-0.25 h	40	NV	Avoidance	static	NV	NV	nominal	satisfactory	Summerfelt and Lewis (1967)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
Unacceptable or Unverified Data													
invertebrate	*Chironomus thummi*	midge	acute	96-98 h	10,253	NOEC	behavioiur	renewal	6.5-8.5	20	measured	NV	Van der Zandt et al. (1994)
invertebrate	*Daphnia magna*	water flea	acute	24 h	>10,000	LC_{50}	mortality	static	8	19	NV	NV	Bringmann and Kuhn (1977b)
invertebrate	*Daphnia magna*	water flea	acute	24 h	>10,000	EC_{50}	lost equilibrium		7.4	25	NV	NV	Bringmann and Kuhn (1982)
invertebrate	*Daphnia magna*	water flea	acute	24 h	>10,000	EC_{50}	immobilization	static	8.3	15-21	NV	NV	Kuhn et al. (1989)
invertebrate	*Daphnia magna*	water flea	acute	24 h	10,000	EC_{100}	lost equilibrium		NV	NV	NV	NV	Bringmann and Kuhn (1982)
invertebrate	*Palaemonetes kadiakensis*	grass shrimp,freshwater prawn	acute	18 h	21,911	LC_{50}	mortality	static	NV	NV	NV	NV	Bowman et al. (1981)
invertebrate	*Daphnia magna*	water flea	acute	48 h	>10,000	EC_{50}	immobilization	static	7.6-8.2	16.3	nominal	NV	Kuhn et al. (1989)
invertebrate	*Asellus intermedius*	aquatic sowbug	acute	96 h	>100	LC_{50}	mortality	static	NV	NV	nominal	NV	Ewell et al. (1986)
invertebrate	*Daphnia magna*	water flea	acute	96 h	>100	LC_{50}	mortality	static	NV	NV	nominal	NV	Ewell et al. (1986)
invertebrate	*Dugesia tigrina*	turbellarian, flatworm	acute	96 h	>100	LC_{50}	mortality	static	NV	NV	nominal	NV	Ewell et al. (1986)
invertebrate	*Gammarus fasciatus*	scud	acute	96 h	>100	LC_{50}	mortality	static	NV	NV	nominal	NV	Ewell et al. (1986)
invertebrate	*Helisoma trivolvis*	ramshorn snail	acute	96 h	>100	LC_{50}	mortality	static	NV	NV	nominal	NV	Ewell et al. (1986)
invertebrate	*Culex restuans*	white dotted mosquito	acute	18 h	20,012	LC_{50}	mortality	static	7.6-8.2	15	nominal	NV	Bowman et al. (1981)
other	*Spirostomum ambiguum*	protozoa	chronic	48 h	36,814	LC_{50}	mortality	static	7.8	10	NV	NV	Nalecz-Jawecki and Sawicki (1999)
other	*Uronema parduczi*	ciliate	acute	20 h	>10,000	NV	growth	NV	6.5	25	NV	NV	Bringmann and Kuhn (1980b)
other	*Anabaena inaequalis*	blue-green algae	chronic	10-14 d	26,800	EC_{50}	growth	static	7.9	10	nominal	NV	Stratton (1987)
other	*Anabaena cylindrica*	blue-green algae	chronic	10-14 d	25,700	EC_{50}	growth	static	NV	25	nominal	NV	Stratton (1987)
other	*Anabaena sp.*	blue-green algae	chronic	10-14 d	31,200	EC_{50}	growth	static	NV	NV	nominal	NV	Stratton (1987)
other	*Anabaena variabilis*	blue-green algae	chronic	10-14 d	31,300	EC_{50}	growth	static	NV	NV	nominal	NV	Stratton (1987)
other	*Navicula pelliculosa*	diatom	chronic	11-18 d	80	NV	growth	static	NV	NV	nominal	NV	Adams et al. (1975)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
other	*Entosiphon sulcatum*	flagellate euglenoid	chronic	72 h	>1,000	NV	growth	static	8.1-8.2	20	nominal	NV	Bringmann and Kuhn (1978a)
other	*Geotrichum candidum*	fungus	acute	4 h	48,060	IC_{50}	glucose uptake	NV	NV	15	nominal	NV	Jacobsen (1995)
other	*Spirostomum ambiguum*	protozoa	chronic	48 h	17,590	EC_{50}	deformation	static	7.04-7.97	12.7	nominal	NV	Nalecz-Jawecki and Sawicki (1999)
other	*Entosiphon sulcatum*	flagellate euglenoid	NV	NV	>10,000	NV	growth	NV	6.5	25	nominal	NV	Bringmann and Kuhn (1979)
other	*Entosiphon sulcatum*	flagellate euglenoid	NV	NV	>10,000	NV	growth	NV	6.5	25	nominal	NV	Bringmann and Kuhn (1981)
other	*Paramecium caudatum*	ciliate	acute	4 h	7,690	LC_{50}	mortality	static	6.2-9	25	nominal	NV	Rajini et al. (1989)
other	*Plankton*	plankton	chronic	4 d	500-20000	NV	population diversity	static	NV	30	nominal	NV	Berard (1996)
other	*Plankton*	plankton	chronic	4 d	500-20000	NV	growth	static	NV	30	nominal	NV	Berard (1996)
other	*Uronema parduczi*	ciliate	NV	NV	>10,000	NV	growth	NV	8.3	15-21	nominal	NV	Bringmann and Kuhn (1981)
plant/alga	*Algae*	algae, algal mat	chronic	11-14 d	80	NV	growth	static	NV	27	nominal	NV	Adams et al. (1975)
plant/alga	*Chlorella sp.*	green algae	chronic	11-20 d	80	NV	growth	static	NV	27	nominal	NV	Adams et al. (1975)
plant/alga	*Chlamydomonas reinhardtii*	green algae	chronic	11-17 d	80	NV	growth	static	NV	27	nominal	NV	Adams et al. (1975)
plant/alga	*Selenastrum capricornutum*	green algae	chronic	11-16 d	7,900	NV	growth	static	7.4	12	nominal	NV	Adams et al. (1975)
plant/alga	*Chlorella pyrenoidosa*	green algae	chronic	10-14 d	28,476	EC_{50}	growth	static	NV	27	nominal	NV	Stratton and Smith (1988)
plant/alga	*Kirchneriella sp.*	green algae	chronic	11-14 d	80	NV	growth	static	NV	NV	nominal	NV	Adams et al. (1975)
plant/alga	*Selenastrum capricornutum*	green algae	chronic	4 d	1,582	NV	growth	NV	8.1-8.2	20	nominal	NV	El Jay (1996)
plant/alga	*Chlorella zofingiensis*	green algae	chronic	48 h	>=16,020	EC80	assimilation efficiency	static	7.04-7.97	19.8	nominal	NV	Weber et al. (1984)
plant/alga	*Chlorococcales*	green algae order	acute	24 h	12,000	EC_{50}	assimilation efficiency	static	6.5-8.5	20	nominal	NV	Krebs (1991)
plant/alga	*Scenedesmus quadricauda*	green algae	NV	NV	8,000	NV	growth	NV	6.5	28	nominal	NV	Bringmann and Kuhn (1979)
plant/alga	*Scenedesmus quadricauda*	green algae	NV	NV	8,000	NV	mortality	static	NV	NV	nominal	NV	Bringmann and Kuhn (1978d)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	weight	flow through	NV	25	measured	NV	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	length	flow through	8	NV	measured	NV	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	vitellogenin	flow through	NV	23	NV	NV	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	vitellogenin	flow through	NV	23	NV	NV	Panter et al. (2002)
vertebrate	*Cyprinus carpio*	carp	acute	48 h	36,000	LC_{50}	mortality	NV	7	20	NV	NV	Nishiuchi and Hashimoto (1967)
vertebrate	*Leuciscus idus melanotus*	carp	acute	48 h	>10,000	LC_{50}	mortality		7.4	25	NV	NV	Juhnke and Luedemann (1978)
vertebrate	*Pimephales promelas*	fathead minnow	acute	48 h	29,700	LC_{50}	mortality	flow through	NV	27	NV	NV	Poirier et al. (1986)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	24 h	>10,000	LC_{50}	mortality	static	7.6-7.7	20-22	NV	NV	Tsuji et al. (1986)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	condition	flow through	NV	NV	NV	NV	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	condition	flow through	NV	NV	NV	NV	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	weight	flow through	NV	NV	NV	NV	Panter et al. (2002)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	chronic	7-21 d	8	NV	condition	flow through	7.8	16.3	nominal	NV	Thorpe et al. (2000)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	chronic	7-21 d	8	NV	organ weight	flow through	NV	27	nominal	NV	Thorpe et al. (2000)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	condition	flow through	NV	23-25	nominal	NV	Panter et al. (2002)
vertebrate	*Semotilus atromaculatus*	creek chub	acute	24 h	8,000	LC0	mortality	static	NV	12	nominal	NV	Gillette et al. (1952)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	vitellogenin	flow through	NV	23	nominal	NV	Panter et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	length	flow through	NV	23	nominal	NV	Panter et al. (2002)
vertebrate	*Lepomis macrochirus*	bluegill	acute	24 h	16,100	EC_{50}	lost equilibrium	flow through	7.04-7.97	19.8	nominal	NV	Poirier et al. (1986)

Table 6. Toxicity of Methanol to Freshwater Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Chemical Analysis	Control Type	Reference
					mg/L					°C			
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	48 h	13,200	EC_{50}	lost equilibrium	flow through	7.7	22	nominal	NV	Poirier et al. (1986)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	48 h	52,000	LC_{50}	mortality	NV	7.2	22.8	nominal	NV	Nishiuchi and Hashimoto (1967)
vertebrate	*Leuciscus idus melanotus*	carp	acute	48 h	>10,000	LC_{50}	mortality		7.4	25	nominal	NV	Juhnke and Luedemann (1978)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	48 h	>10,000	LC_{50}	mortality	static	7.53	25.4	nominal	NV	Tsuji et al. (1986)
vertebrate	*Pimephales promelas*	fathead minnow	acute	72 h	28,400	LC_{50}	mortality	flow through	NV	27	nominal	NV	Call et al. (1983)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-14 d	0	NV	genotoxicity	flow through	NV	18-May	nominal	NV	Halm et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-14 d	0	NV	size	flow through	NV	18-May	nominal	NV	Halm et al. (2002)
vertebrate	*Pimephales promelas*	fathead minnow	acute	96 h	>100	LC_{50}	mortality	static	7.8	20	nominal	NV	Ewell et al. (1986)
vertebrate	*Oryzias latipes*	medaka, high-eyes	acute	48 h	>10,000	LC_{50}	mortality	static	NV	20-25	nominal	NV	Tsuji et al. (1986)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	chronic	7-21 d	8	NV	vitellogenin	flow through	NV	NV	nominal	NV	Thorpe et al. (2000)
vertebrate	*Pimephales promelas*	fathead minnow	chronic	4-21 d	<=79	NV	length	flow through	NV	NV	nominal	NV	Panter et al. (2002)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	65 mi	120	LOEC	respiration	flow through/	7.8	20	nominal	NV	Baldwin et al. (1994)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	14 d	8	NV	vitellogenin	flow through	NV	NV	nominal	NV	Thorpe et al. (2001)
vertebrate	*Oncorhynchus mykiss*	rainbow trout	acute	24 h	13,200	EC_{50}	lost equilibrium	flow through	6.9-7.8	NV	nominal	NV	Poirier et al. (1986)

Notes:

NV = not reported in the abstract and not verified in this literature search

Table 7. Toxicity of Methanol to Marine Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Salinity	Chemical Analysis	Control Type	Reference
					mg/L					°C	ppt			
Primary Data														
invertebrate	*Artemia salina*	brine shrimp	acute	1 h	1,000,000	NV	histological changes	static	NV	20	NV	m	s	Vismara (1998)
invertebrate	*Mytilus edulis*	blue mussel	acute	96 h	7,960	NOEC	immobilization	flow through	NV	21	NV	m	s	Helmstetter et al. (1996)
invertebrate	*Mytilus edulis*	blue mussel	acute	96 h	16,700	LC_{50}	mortality	flow through	7.04-7.97	12.7	NV	m	s	Helmstetter et al. (1996)
invertebrate	*Mytilus edulis*	blue mussel	acute	96 h	15,200	LC_{50}	mortality	flow through	7.04-7.97	19.8	NV	m	s	Helmstetter et al. (1996)
invertebrate	*Nitocra spinipes*	harpacticoid copepod	acute	96 h	12,000	LC_{50}	mortality	static	6.5-8.5	20	NV	m	s	Linden et al. (1979)
invertebrate	*Nitocra spinipes*	harpacticoid copepod	acute	96 h	12,000	LC_{50}	mortality	static	6.5-8.5	20	NV	m	s	Bengtsson et al. (1984)
invertebrate	*Crangon crangon*	sand shrimp	acute	96 h	1,700	LC_{50}	mortality	renewal	6.2-9	25	NV	m	s	Portmann and Wilson (1971)
invertebrate	*Artemia salina*	brine shrimp	acute	48 h	11,855	LOEC	emergence	NV	6.5-8.5	20	NV	m	s	Vismara (1998)
vertebrate	*Agonus cataphractus*	hooknose	acute	48 h	10,000-33,000	LC_{50}	mortality	renewal	NV	21-25	14-Dec	m	s	Portmann and Wilson (1971)
vertebrate	*Alburnus alburnus*	bleak	acute	96 h	28,000	LC_{50}	mortality	static	7	27	NV	m	s	Bengtsson et al. (1984)
vertebrate	*Alburnus alburnus*	bleak	acute	96 h	>28,000	LC_{50}	mortality	static	NV	NV	NV	m	s	Linden et al. (1979)
Secondary Data														
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	10 d	79	NV	mortality	renewal	NV	17-20	30	n	s	Hutchinson et al. (1999)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	10 d	79	NV	sex ratio	renewal	NV	17-20	36	n	s	Hutchinson et al. (1999)

Table 7. Toxicity of Methanol to Marine Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Salinity	Chemical Analysis	Control Type	Reference
					mg/L					°C	ppt			
invertebrate	*Artemia salina*	brine shrimp	acute	24 h	43,520	LC_{50}	mortality	static	NV	15	NV	n	s	Calleja and Persoone (1992)
invertebrate	*Artemia salina*	brine shrimp	acute	24 h	43,520	LC_{50}	mortality	NV	NV	15	NV	n	s	Calleja et al. (1994)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	10 d	79	NV	mortality	renewal	NV	NV	NV	n	s	Hutchinson et al. (1999)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	10 d	79	NV	sex ratio	renewal	NV	NV	NV	n	s	Hutchinson et al. (1999)
invertebrate	*Artemia salina*	brine shrimp	acute	24 h	901	LC_{50}	mortality	static	8.1-8.2	20	34.75-35.5	n	s	Barahona-Gomariz et al. (1994)
invertebrate	*Artemia salina*	brine shrimp	acute	24 h	1,101	LC_{50}	mortality	static	8.1-8.2	20	34.75-35.5	n	s	Barahona-Gomariz et al. (1994)
invertebrate	*Artemia salina*	brine shrimp	acute	24 h	1,579	LC_{50}	mortality	static	8.1-8.2	20	34.75-35.5	n	s	Barahona-Gomariz et al. (1994)
invertebrate	*Cerastoderma edule*	cockle	acute	48 h	1,000	LC_{50}	mortality	renewal	8.1-8.2	20	34.75-35.5	n	s	Portmann and Wilson (1971)
invertebrate	*Artemia salina*	brine shrimp	acute	48 h	6,728	NOEC	emergence	NV	6.2-9	25	NV	n	s	Vismara (1998)
invertebrate	*Crangon crangon*	sand shrimp	acute	48 h	2,500	LC_{50}	mortality	renewal	6.2-9	25	NV	n	s	Portmann and Wilson (1971)
invertebrate	*Mytilus edulis*	blue mussel	acute	4-12 h	79	NV	respiration	flow through	NV	27	30	n	s	Lindblad et al. (1986)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	1-21 d	79	NV	survival	renewal	NV	NV	NV	n	s	Hutchinson et al. (1999)
other	*Brachionus plicatilis*	rotifer	acute	24 h	51,840	LC_{50}	mortality	static	NV	24	NV	n	s	Calleja and Persoone (1992)
other	*Anacystis aeruginosa*	blue-green algae	chronic	8 d	530	NV	growth	static	6.9-7.5	14.9-15.5	NV	n	s	Bringman and Kuhn (1978c)

Table 7. Toxicity of Methanol to Marine Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Salinity	Chemical Analysis	Control Type	Reference
					mg/L					°C	ppt			
vertebrate	*Sciaenops ocellatus*	red drum	acute	0.33 h	8,010	NV	mortality (hatching)	static	7.6	20	NV	n	s	Robertson et al. (1988)
vertebrate	*Agonus cataphractus*	hooknose	acute	96 h	10,000-33,000	LC_{50}	mortality	renewal	NV	21-25	14-Dec	n	s	Portmann and Wilson (1971)
vertebrate	*Rivulus marmoratus*	rivulus	chronic	60 d	475	NV	sex ratio	renewal	NV	16-Nov	NV	n	s	Tanaka and Grizzle (2002)
Unacceptable or Unverified Data														
invertebrate	*Artemia salina*	brine shrimp	acute	48 h	46,778	EC_{50}	emergence	NV	NV	15	NV	NV	NV	Vismara (1998)
invertebrate	*Cerastoderma edule*	cockle	acute	96 h	3,300-10,000	LC_{50}	mortality	renewal	7.5	25	NV	NV	NV	Portmann and Wilson (1971)
invertebrate	*Artemia salina*	brine shrimp	acute	24 h	>10,000	LC_{50}	mortality	static	NV	19.5-20.5	NV	NV	NV	Price et al. (1974)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	acute	1-5 d	79	NV	development	renewal	NV	17-20	36	n	NV	Hutchinson et al. (1999)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	acute	1-5 d	79	NV	development	renewal	NV	17-20	36	n	NV	Hutchinson et al. (1999)
invertebrate	*Artemia salina*	brine shrimp	acute	48 h	48,060	LC_{50}	mortality	NV	NV	15	NV	n	NV	Vismara (1998)
invertebrate	*Mytilus edulis*	blue mussel	acute	89 h	30,000	NV-LETH	mortality	flow through	NV	NV	NV	n	NV	Helmstetter et al. (1996)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	1-21 d	79	NV	maturity	renewal	NV	NV	NV	n	NV	Hutchinson et al. (1999)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	1-21 d	79	NV	sex ratio	renewal	NV	NV	NV	n	NV	Hutchinson et al. (1999)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	1-21 d	79	NV	fecundity	renewal	NV	NV	NV	n	NV	Hutchinson et al. (1999)
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	10 d	79	NV	progeny	renewal	NV	17-20	30	n	NV	Hutchinson et al. (1999)

Table 7. Toxicity of Methanol to Marine Aquatic Life

Biota Type	Scientific Name	Common Name	Study Type	Test Duration	Concentration	Endpoint	Effect	Exposure Type	pH	Temperature	Salinity	Chemical Analysis	Control Type	Reference
					mg/L					°C	ppt			
invertebrate	*Tisbe battagliai*	harpacticoid copepod	chronic	10 d	79	NV	progeny	renewal	NV	17-20	36	n	NV	Hutchinson et al. (1999)
invertebrate	*Mytilus edulis*	blue mussel	acute	13.5 h	50,000-100,000	NV-LETH	mortality	flow through	NV	NV	NV	n	NV	Helmstetter et al. (1996)
other	*Chaetoceros gracilis*	diatom	acute	1-240 mi	39,550-237,300	NV	growth	static	NV	NV	35	n	NV	Canavate and Lubian (1994)
other	*Isochrysis galbana*	haptophyte	acute	1-240 mi	39,550-237,300	NV	growth	static	NV	25	NV	n	NV	Canavate and Lubian (1994)
other	*Rhodomonas baltica*	cryptomonad	acute	1-240 mi	39,550-237,300	NV	growth	static	NV	NV	NV	n	NV	Canavate and Lubian (1994)
other	*Tetraselmis chuii*	prasinophyte	acute	1-240 mi	39,550-237,300	NV	growth	static	NV	NV	NV	n	NV	Canavate and Lubian (1994)
other	*Anacystis aeruginosa*	blue-green algae	NV	NV	530	NV	mortality	static	6.9-7.5	14.9-15.5	NV	n	NV	Bringman and Kuhn (1978d)
plant/alga	*Nannochloris atomus*	microalgae	acute	1-240 mi	39,550-237,300	NV	growth	static	NV	25	15	n	NV	Canavate and Lubian (1994)
plant/alga	*Nannochloropsis gaditana*	microalgae	acute	1-240 mi	39,550-237,300	NV	growth	static	NV	25	NV	n	NV	Canavate and Lubian (1994)
vertebrate	*Rivulus marmoratus*	rivulus	chronic	60 d	475	NV	gamete production	renewal	6.9-7.5	14.9-15.5	NV	n	NV	Tanaka and Grizzle (2002)

Notes:

NV = not reported in the abstract and not verified in this literature search

chemical analysis: m = measured, n = nominal

control type: c = concurrent; s = satisfactory

Table 8. Toxicity of Methanol to Mammalian Species – Selected Studies

Study Type	Species	Route	NOAEL/ NOAEC	LOAEL/ LOAEC/ LPTD	LD_{50}/ LC_{50}	Duration/ Exposure	Endpoint	Reference
Acute								
acute	human	oral			300-1,000 mg/kg bw (LPLD)	single	acidosis, ocular toxicity	WHO (1997)
acute	rhesus monkey	oral			3,000 mg/kg bw (LPLD)	single	CNS Depression, acidosis, and ocular toxicity, death	Gilger and Potts (1955)
acute	rhesus monkey	oral			7,000 mg/kg bw (LPLD)	single	CNS effects, acidosis, death	Cooper & Felig (1961)
acute	rhesus monkey; pigtail monkey	oral			3,000 mg/kg bw (LPLD)	single	CNS effects, acidosis, respiratory effects, death	McMartin et al. (1975); Clay et al. (1975)
acute	rat	oral			6,200-13,000 mg/kg bw	single	CNS effects, acidosis, respiratory effects, death	Kimura et al. (1971); Welch and Slocum (1943); Gliger and Potts (1955); Deichmann (1948); Smyth et al. (1941)
acute	mouse	oral			7,300 - 10,000 mg/kg bw	single	CNS effects, acidosis, respiratory effects, death	Smith and Taylor (1982)
acute	rabbit	oral			7,000 mg/kg bw (LPLD)	single	CNS effects, acidosis, respiratory effects, death	Gliger and Potts (1955)
acute	dog	oral			8,000 mg/kg bw (LPLD)	single	CNS effects, acidosis, respiratory effects, death	Gliger and Potts (1955)
acute	guinea-pig	dermal	50% methanol				no irritation or sensitization	BASF, 1979
acute	rabbit	occular		100 uL		single	significant conjunctivitis	Jacobs, 1990

Table 8. Toxicity of Methanol to Mammalian Species – Selected Studies

Study Type	Species	Route	NOAEL/ NOAEC	LOAEL/ LOAEC/ LPTD	LD_{50}/ LC_{50}	Duration/ Exposure	Endpoint	Reference
Chronic and Sub-Chronic								
chronic	rat	inhalation	100 ppm	1,000 ppm		12 months	reduced weight gain; small (not significant) gain in relative weight of liver and spleen in increased body weight	NEDO, 1987; Katoh, 1989
chronic	mouse	inhalation	100 ppm	1,000 ppm		12 months		NEDO, 1987; Katoh, 1989
chronic	monkey	inhalation	1,000 ppm			29 months	no dose-related effects	NEDO, 1982
sub-chronic	rat	inhalation	5,000 ppm			intermittent, 4 weeks	no toxic effects except for mild irritation of the upper respiratory tract	Andrews et al., 1987
sub-chronic	rat	inhalation	10,000 ppm			intermittent, 6 weeks	no toxic effects on respiratory system	White et al., 1983
sub-chronic	cynomolgus monkeys	inhalation	10,000 ppm			intermittent, 4 weeks	no irritation of the upper respiratory tract; no ocular effects	Andrews et al., 1987
sub-chronic	rat	oral	500 mg/kg bw/day	2,500 mg/kg bw/day		90 days	elevated SGPT, SAP and reduced brain weight; no effect on body weight gain, food consumption, gross or microscopic evaluations	U.S. EPA (1986)
sub-chronic	dog	inhalation				NV	study reviewed by U.S. EPA as not suitable for deriving an RfD.	Sayers et al. (1942)
Reproduction and Developmental								
developmental	rat	inhalation	5,000 ppm	10,000 ppm		day 1-19 of pregnancy	reduced fetal weight	Nelson et al. (1985)
developmental	rat	inhalation	10,000 ppm	20,000 ppm		day 1-19 of pregnancy	maternal – neurological effects (unsteady gait on initial exposure; no effect on food intake or body weight gain)	Nelson et al. (1985)
developmental	mouse	inhalation	1,000 ppm	2,000 ppm		day 6-15 of pregnancy	teratology – increased incidence of cervical ribs in fetus	Rogers et al. (1993)
developmental	mouse	inhalation	15,000 ppm			day 6-15 of pregnancy	maternal – no effect (unsteady gait on initial exposure; no effect on food intake or body weight gain)	Rogers et al. (1993)
reproductive	rat	inhalation	800 ppm			20 h/day, 7 days/weel for 13 weeks	no effect on structure of male reproductive system	Lee et al. (1991)
reproductive	rat	inhalation	1,500 mg/L blood methanol level				no effect on male hormones	Cooper et al. (1992)

Table 8. Toxicity of Methanol to Mammalian Species – Selected Studies

Study Type	Species	Route	NOAEL/ NOAEC	LOAEL/ LOAEC/ LPTD	LD_{50}/ LC_{50}	Duration/ Exposure	Endpoint	Reference
Carcinogenicity and Genotoxicity								
carcinogenicity	mouse	dermal				50 week exposure; lifetime observation	no cancer effects	Lijinsky et al., 1991
carcinogenicity	mouse, rat	inhalation	1,000 ppm			24 months	no carcinogenic effects	NEDO, 1987; Katoh, 1989

Notes:

NV = not reported in the abstract and not verified in this literature search

dw = drinking water

LPLD = lowest published lethal dose

LPTD = lowest published toxic dose

NOAEL/NOAEC = no observed adverse effect level/concentration

LOAEL/LOAEC = lowest observed adverse effect level/concentration

LD_{50}/LC_{50} = lethal dose/concentration for 50% kill

Table 9. Chemical-Specific Parameter Values for Methanol

Parameter	Unit	Value	Rationale
Human Toxicity			
Tolerable Daily Intake (oral exposure)	mg/kg-bw/day	0.5	see Section 6.5
Tolerable Concentration (inhalation exposure)	mg/m^3	2.2	see Section 6.5
Human Background Exposure			
Estimated daily intake	mg/kg-bw/day	0.4	see Section 2.6
Ambient air concentration	mg/m^3	0.04	see Section 2.6
Background soil concentration	mg/kg	0	see Section 2.6
Soil allocation factor	-	0.2	see Section 9.1
Water allocation factor	-	0.2	see Section 9.1
Human Adsorption			
Adsorption factor - gut	-	1.0	assumed
Adsorption factor - skin	-	1.0	assumed
Adsorption factor - lung	-	1.0	assumed
Chemical and Physical Properties			
Soil Organic Carbon/Water Partition Coefficient (Koc)	L/kg	0.27	see Table 2
Dimensionless Henry's law coeffcient	(mg/L)/(mg/L)	0.0002	see Table 2
Dynamic viscosity of vapour	g/cm.s	1.73×10^{-4}	AENV (2007)
Diffusion coefficient in air	cm^2/s	0.15	ORNL (2007)
Degradation			
Degradation half life (saturated)	days	245	see Section 3.4

Table 10. Human Receptor Characteristics

Parameter	Symbol	Unit	Toddler	Adult
Body Weight	BW	kg	16.5	70.7
Air Inhalation Rate	IR	m^3/d	9.3	15.8
Soil Inhalation Rate	IR_S	kg/d	7.1×10^{-9}	1.2×10^{-8}
Water Ingestion Rate	WIR	L/d	0.6	1.5
Soil Ingestion Rate	SIR	kg/d	0.00008	0.00002
Skin Surface Area				
- Hands	SA_H	m^2	0.043	0.089
- Other	SA_O	m^2	0.258	0.25
Dermal Loading to Skin				
- Hands	DL_H	kg/m^2-event	0.001	0.001
- Other	DL_O	kg/m^2-event	0.0001	0.0001
Dermal Exposure Frequency	EF	events/d	1	1
Exposure Term, agricultural and residential/parkland	ET	-	1	1
Exposure Term, commercial and industrial	ET	-	0.2747	0.2747
Exposure Term, agricultural and residential/parkland	ET_1	-	1	1
Exposure Term, commercial and industrial	ET_1	-	0.6593	0.6593
Exposure Term, agricultural and residential/parkland	ET_2	-	1	1
Exposure Term, commercial and industrial	ET_2	-	0.4167	0.4167

Notes:

All parameter values from AENV (2007a)

Table 11. Soil and Hydrogeological Parameters

Parameter	Symbol	Unit	Fine Soil	Coarse Soil
Soil Bulk Density	ρ_B	*kg/L*	1.4	1.7
Soil Total Porosity	θ_t	cm^3/cm^3	0.47	0.36
Soil Moisture-Filled Porosity	θ_w	cm^3/cm^3	0.168	0.119
Soil Vapour-Filled Porosity	θ_a	cm^3/cm^3	0.302	0.241
Soil Vapour-Filled Porosity in Floor Cracks	θ_a	cm^3/cm^3	0.47	0.36
Gravimetric Water Content	MC	*g/g*	0.12	0.07
Fraction of Organic Carbon	f_{oc}	*mass/mass*	0.005	0.005
Saturated Hydraulic Conductivity	K	*m/y*	32	320
Hydraulic Gradient	i	*m/m*	0.028	0.028
Recharge (Infiltration) Rate	I	*m/y*	0.012	0.06
Soil Permeability to Vapour Flow	k_v	cm^2	10^{-9}	$6x10^{-8}$

Notes:
All parameter values from AENV (2007a)

Table 12. Site Characteristics

Parameter	Symbol	Unit	Value
Contaminant Source Width	Y	m	10
Contaminant Source Length	X	m	10
Contaminant Source Depth	Z	m	3
Distance to Surface Water	x	m	10
Distance to Potable Water User	x	m	0
Distance to Agricultural Water User	x	m	0
Distance from Contamination to Building Slab	L_T	cm	30
Depth to Groundwater (water table)	d	m	3
Depth of unconfined aquifer	d_a	m	5

Notes:
All parameter values from AENV (2007a)

Table 13. Building Parameters

Parameter	Symbol	Unit	Residential Basement	Residential Slab-on-Grade	Commercial Slab-on-Grade
Building Length	L_B	*cm*	1,225	1,225	2,000
Building Width	W_B	*cm*	1,225	1,225	1,500
Building Height (including basement)	H_B	*cm*	360	360	300
Area of Substructure	A_B	cm^2	$2.7x10^6$	$1.5x10^6$	$3.0x10^6$
Thickness of Floor Slab	L_{crack}	*cm*	11.25	11.25	11.25
Depth of Floor Slab Below Ground	Z_{crack}	*cm*	244	11.25	11.25
Distance from Source to Slab:	L_T	*cm*			
surface soil			30	30	30
subsoil			30	139	139
Crack Area	A_{crack}	cm^2	994.5	994.5	1,846
Crack Length	X_{crack}	*cm*	4,900	4,900	7,000
Air Exchange Rate	ACH	*exch/hr*	0.5	0.5	0.9
Pressure Differential	ΔP	$g/cm.s^2$	40	40	20

Notes:
All parameter values from AENV (2007a)

Table 14. Surface Water Quality Guidelines for Methanol

Water Use	Guideline Value (mg/L)
Human drinking water ("Source Guidance Value for Groundwater")	4.5
Freshwater aquatic life	1.5
Irrigation [1]	n/c
Livestock watering [2]	n/c
Wildlife watering [3]	n/c

Notes:
n/c = not calculated

1. *guideline protective of irrigation not calculated; not expected to be an issue due to volatility and degradability of methanol.*
2. *guideline not calculated due to the lack of toxicity information for livestock species.*
3. *guideline not calculated due to the lack of toxicity information for wildlife species.*

Table 15. Soil Remediation Guidelines for Methanol - Coarse Soil

	Guideline Value (mg/kg)				
Land Use:	**Natural Area**	**Agricultural**	**Residential**	**Commercial**	**Industrial**
Overall Guideline	**0.75**	**0.75**	**0.75**	**0.75**	**0.75**
Human Exposure Pathways					
Direct soil contact	n/a	2,000	2,000	3,500	16,000
Vapour inhalation	n/a	150	150	2,000	2,000
Protection of domestic use aquifer	10	10	10	10	10
Produce, milk and meat check [1]	n/c	n/c	n/c	n/c	n/c
Off-site migration [2]	n/a	n/a	n/a	n/c	n/c
Ecological Exposure Pathways					
Direct soil contact	2,500	2,500	2,500	3,000	3,000
Nutrient and Energy cycling check [3]	n/c	n/c	n/c	n/c	n/c
Livestock soil and food ingestion [4]	n/c	n/c	n/c	n/c	n/c
Protection of freshwater aquatic life	0.75	0.75	0.75	0.75	0.75
Off-site migration [2]	n/a	n/a	n/a	n/c	n/c
Management Limit	750	750	750	750	750

Notes:
n/a = exposure pathway not applicable in this scenario.
n/c = not calculated

1. *produce, meat and milk check not calculated - methanol not expected to accumulate in produce, milk, or meat.*
2. *offsite migration not considered a concern given the volatility and degradability of methanol.*
3. *Nutrient and energy cycling check not calculated - insufficient data*
4. *Livestock soil and food ingestion not expected to be a concern, methanol expected to be lost rapidly from surface soil, and not accumulate into fodder.*

Table 16. Soil Remediation Guidelines for Methanol - Fine Soil

	Guideline Value (mg/kg)				
Land Use:	**Natural Area**	**Agricultural**	**Residential**	**Commercial**	**Industrial**
Overall Guideline	**9.0**	**9.0**	**9.0**	**9.0**	**9.0**
Human Exposure Pathways					
Direct soil contact	n/a	2,000	2,000	3,500	16,000
Vapour inhalation	n/a	3,500	3,500	25,000	25,000
Protection of domestic use aquifer	9.0	9.0	9.0	9.0	9.0
Produce, milk and meat check [1]	n/c	n/c	n/c	n/c	n/c
Off-site migration [2]	n/a	n/a	n/a	n/c	n/c
Ecological Exposure Pathways					
Direct soil contact	2,500	2,500	2,500	3,000	3,000
Nutrient and Energy cycling check [3]	n/c	n/c	n/c	n/c	n/c
Livestock soil and food ingestion [4]	n/c	n/c	n/c	n/c	n/c
Protection of freshwater aquatic life	20	20	20	20	20
Off-site migration [2]	n/a	n/a	n/a	n/c	n/c
Management Limit	750	750	750	750	750

Notes:
n/a = exposure pathway not applicable in this scenario.
n/c = not calculated

1. *produce, meat and milk check not calculated - methanol not expected to accumulate in produce, milk, or meat.*
2. *offsite migration not considered a concern given the volatility and degradability of methanol.*
3. *Nutrient and energy cycling check not calculated - insufficient data*
4. *Livestock soil and food ingestion not expected to be a concern, methanol expected to be lost rapidly from surface soil, and not accumulate into fodder.*

Table 17. Groundwater Remediation Guidelines for Methanol

	Guideline Value (mg/L)				
Land Use:	**Natural Area**	**Agricultural**	**Residential**	**Commercial**	**Industrial**
Lowest Guideline (Coarse)	**2**	**2**	**2**	**2**	**2**
Lowest Guideline (Fine)	**4.5**	**4.5**	**4.5**	**4.5**	**4.5**
Water Use					
Potable groundwater	4.5	4.5	4.5	4.5	4.5
Vapour inhalation from groundwater					
Coarse soil	n/a	2,000	2,000	30,000	30,000
Fine soil	n/a	30,000	30,000	200,000	200,000
Groundwater protective of eco-contact [1]					
Coarse soil	n/c	n/c	n/c	n/c	n/c
Fine soil	n/c	n/c	n/c	n/c	n/c
Groundwater protective of freshwater aquatic life					
Coarse soil	2	2	2	2	2
Fine soil	45	45	45	45	45
Groundwater used for irrigation [2]	n/c	n/c	n/c	n/c	n/c
Groundwater used for livestock watering [3]	n/c	n/c	n/c	n/c	n/c
Groundwater used for wildlife watering [4]	n/c	n/c	n/c	n/c	n/c

Notes:
n/a = water use not applicable in this scenario.
n/c = not calculated
1. *see section 12.1.2*
2. *groundwater protective of irrigation not calculated; not expected to be an issue due to volatility and degradability of methanol.*
3. *Livestock watering groundwater guideline not calculated due to the lack of toxicity information for livestock species.*
4. *Wildlife watering groundwater guideline not calculated due to the lack of toxicity information for wildlife species.*

Table 18. Flammable and Non-Flammable Methanol Concentrations in Soil

Sample #	Location	Distance Along Trench (m)	Date Collected	Flammability	Methanol (mg/kg)
19	Area 3 Trench	1m	14-Oct-05	flame	12,700
20	Area 3 Trench	2m	14-Oct-05	flame	15,900
21	Area 3 Trench	3m	14-Oct-05	flame	14,900
22	Area 3 Trench	3.5m	14-Oct-05	flame	9,310
23	Area 3 Trench	3.75m	14-Oct-05	flame	10,700
24	Area 3 Trench	4.0m	14-Oct-05	no flame	7,460
25	Area 3 Trench	4.5m	14-Oct-05	no flame	13,700
26	Area 3 Trench	5.0m	14-Oct-05	no flame	6,390
27	Area 3 Trench	6.0m	14-Oct-05	no flame	3,990
28	Area 3 Trench	7.0m	14-Oct-05	no flame	80
29	Area 3 Trench	8.0m	14-Oct-05	no flame	48
30	Area 3 Trench	9.0m	14-Oct-05	no flame	53

FIGURES

Figure 1. Major Uses of Methanol

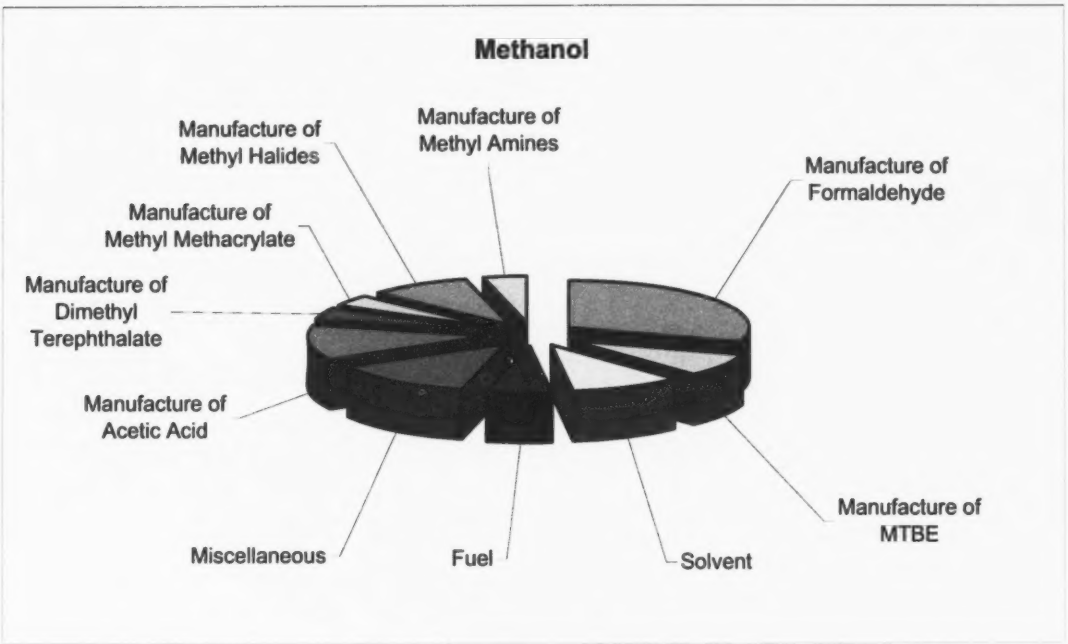


Figure 2. Methanol Biodegradation as a Function of Test Duration

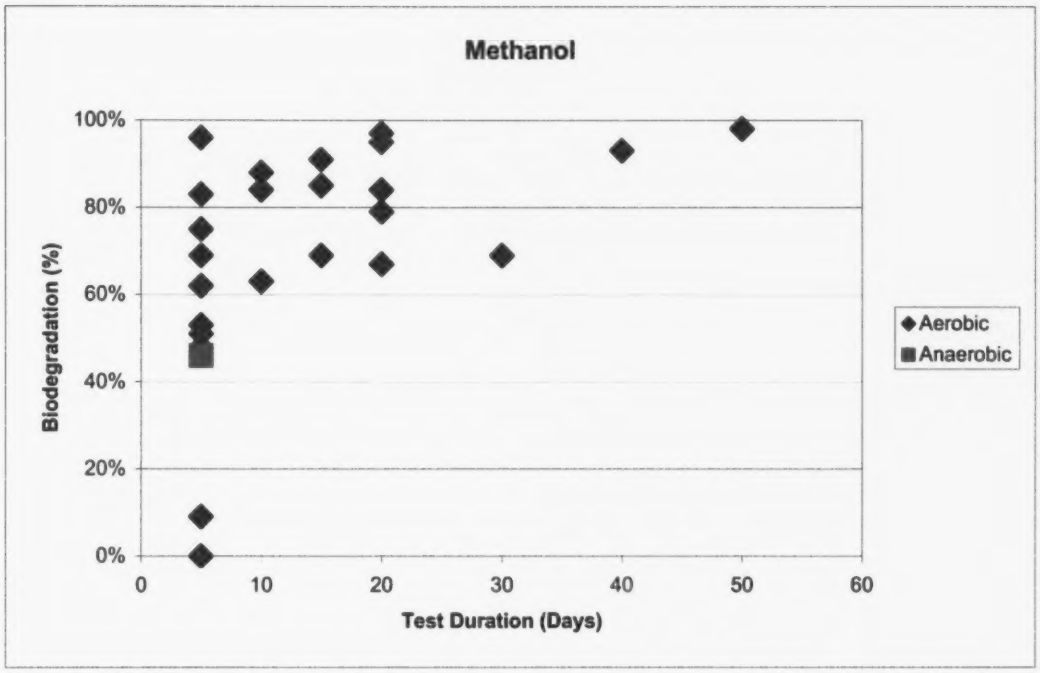
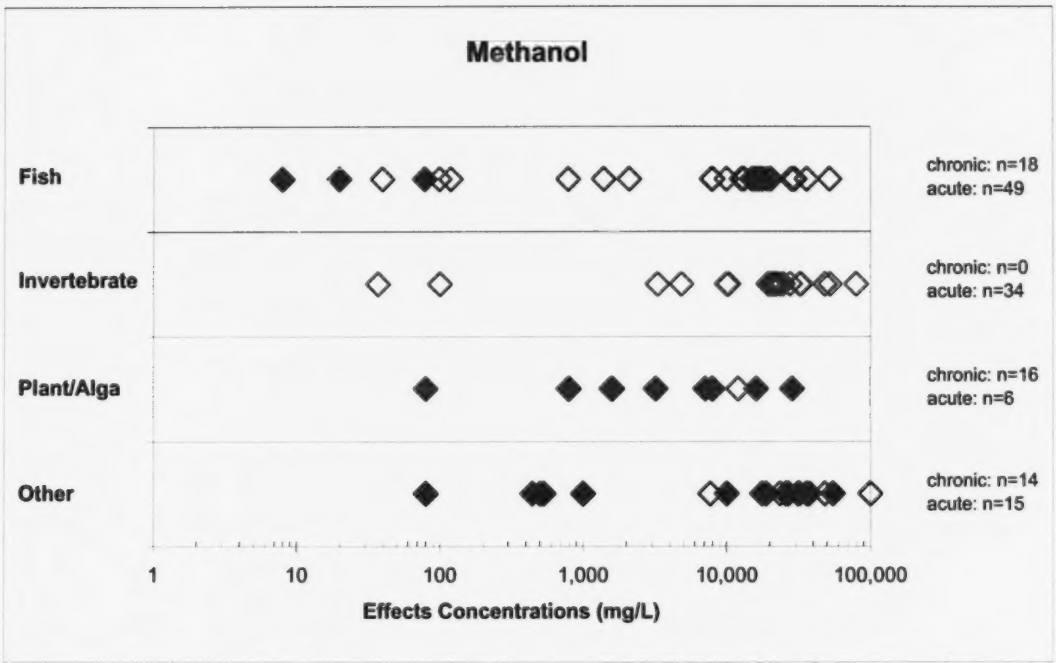
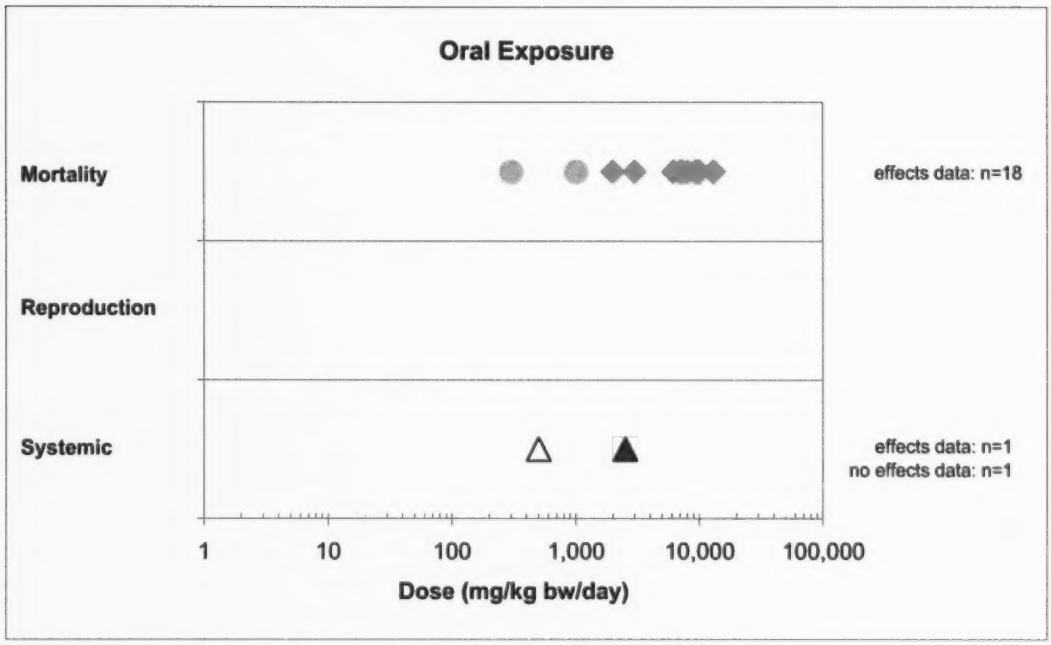


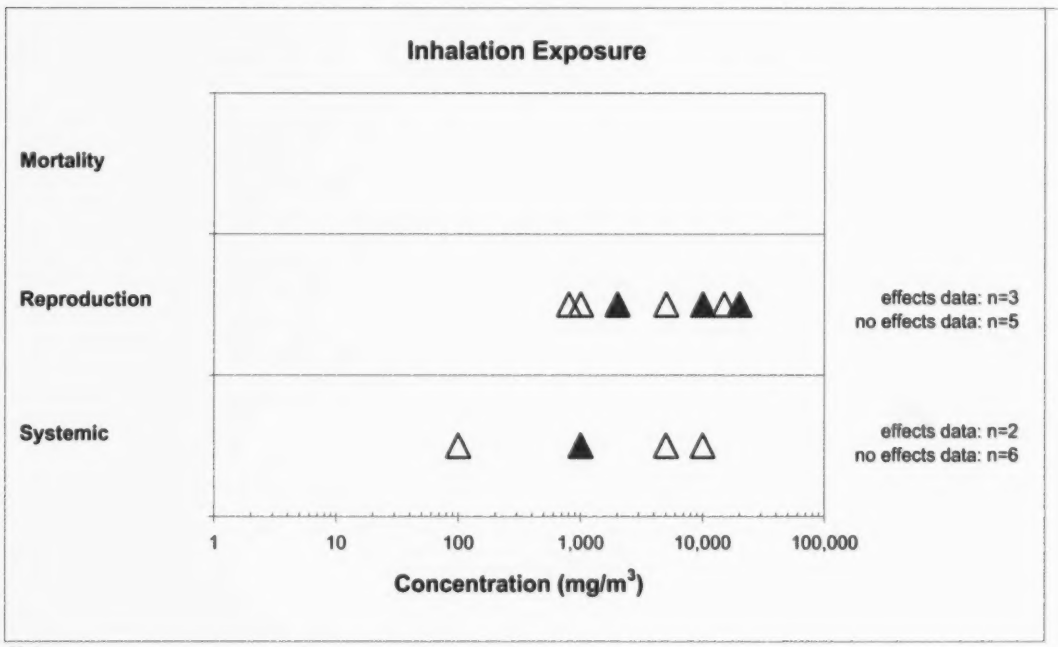
Figure 3. Effects Concentrations of Methanol to Freshwater Aquatic Organisms



Notes:
Solid Symbol = Chronic
Hollow Symbol = Acute

Figure 4. Toxicity of Methanol to Mammalian Species





Notes:

Diamond = Animal Study, Acute
Triangle = Animal Study, (Sub-)Chronic
Circle = Human Data

Solid Symbol = Effects
Hollow Symbol = No Effect